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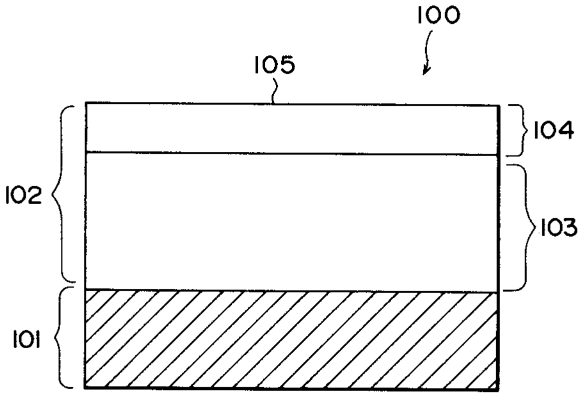
(54) **Electrophotographic light-receiving member.**

(57) To provide an electrophotographic light-receiving member having a good initial-stage electrophotographic performance and also having a good durability especially in an environment of low humidity, the light-receiving member comprises a support 101, a photoconductive layer 103 formed on the support and formed of a non-monocrystalline material mainly composed of silicon atoms, and a surface layer 104 formed of a non-monocrystalline material constituted of silicon atoms, carbon atoms, nitrogen atoms and hydrogen atoms in which silicon atoms having at least one bond to a carbon atom are in a percentage of at least 50 atom% based on the whole silicon atoms in the surface layer.

FIG. 1



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BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to an electrophotographic light-receiving member having a sensitivity to electromagnetic waves such as light (which herein refers to light in a broad sense and indicates ultraviolet rays, visible rays, infrared rays, X-rays, γ-rays, etc.).

Related Background Art

In the field of image formation, photoconductive materials capable of a forming light-receiving layer in an electrophotographic light-receiving member are required to have properties such that they are highly sensitive, have a high SN ratio, have absorption spectra suited to spectral characteristics of electromagnetic waves to be radiated, have a high response to light, have the desired dark resistance and are harmless to human bodies when used.

Photoconductive materials having good properties in these respects include amorphous silicon (hereinafter "A-Si"). For example, U.S. Patent No. 4,265,991 discloses its application in electrophotographic light-receiving members.

Japanese Patent Application Laid-open No. 57-115556 also discloses a technique in which a surface barrier layer formed of a non-photoconductive amorphous material containing silicon atoms and carbon atoms is provided on a photoconductive layer formed of an amorphous material mainly composed of silicon atoms, in order to achieve improvements in photoconductive members having a photoconductive layer formed of an A-Si deposited film, in respect of their electrical, optical and photoconductive properties such as dark resistance, photosensitivity and response to light and service environmental properties such as moisture resistance and also in respect of stability with time.

U.S. Patent No. 4,788,120 discloses a technique in which a surface layer employs an amorphous material containing silicon atoms, carbon atom and 41 to 70 atom% of hydrogen atoms as constituents.

Japanese Patent Application Laid-open No. 54-145537 also discloses an electrophotographic image-forming member comprising a support, an amorphous silicon photoconductive layer and a surface coat layer formed of silicon dioxide, silicon nitride or silicon oxynitride.

Japanese Patent Application Laid-open No. 3-64466 discloses to form an amorphous silicon film by glow discharge decomposition of silane gas at applied voltages with frequencies of 13.56 MHz, 27.12 MHz and 40.68 MHz to produce devices such as photosensitive drums.

These techniques have brought about improvements in electrical, optical and photoconductive properties, service environmental properties and durability of electrophotographic light-receiving members, and also have made it possible to improve image quality levels.

U.S. Patent No. 4,659,639 also discloses a technique concerning a photosensitive member on which a light-transmissive insulating overcoat layer containing amorphous silicon, carbon, oxygen and fluorine is superposingly formed.

Meanwhile, there is a rapid progress in making electrophotographic apparatus have higher speed and higher durability. In addition, they are required to be improved in reliability of component parts so that service cost can be decreased and to decrease the repetition of maintenance service. Under such circumstances, it has now become possible to continue repeated use of electrophotographic light-receiving members over a longer period of time than ever in various environments without maintenance by servicemen.

In such a situation, the actual state of affairs is that there is room for improvements also in conventional electrophotographic light-receiving members.

In particular, their repeated use at a high speed for a long time may cause a phenomenon in which toner adhers on the white ground around images (i.e., fog may occur), often resulting in images with characters hard to read in an extreme case.

Such phenomena become remarkable especially when a reverse development system is employed in digital type copying machines that utilize laser light.

Positive development type copying machines have been hitherto prevalent and there have been not so many digital ones. Also, fog is relatively hard to become conspicuous in line copies of letter or character originals. Hence, such phenomena have not so seriously come into question. However, with spread of digital type color copying machines, such phenomena are now pointed out as a great problem that causes a lowering of image quality, and it has become necessary to immediately solve the problem.

SUMMARY OF THE INVENTION

The present invention was made in order to solve the problems involved in electrophotographic light-receiving members having the conventional light-receiving layer formed of A-Si as stated above.

That is, an object of the present invention is to provide an electrophotographic light-receiving member having a light-receiving layer formed of a non-monocrystalline material mainly composed of silicon atoms, that is substantially always stable almost without dependence of electrical, optical and photoconductive properties on service environments, has a superior resistance to fatigue by light, has superior durability and moisture resistance without causing any deterioration when repeatedly used, can be almost free from residual potential and also can achieve a good image quality.

The above object of the present invention can be achieved by an electrophotographic light-receiving member having at least a support, a photoconductive layer showing a photoconductivity, formed on the support and formed of a non-monocrystalline material mainly composed of a silicon atom and containing at least one of a hydrogen atom and a halogen atom, and a non-monocrystalline layer (a surface layer) formed at the outermost surface, containing at least a silicon atom, a carbon atom, a nitrogen atom and a hydrogen atom, wherein the non-monocrystalline layer comprises non-monocrystals in which silicon atoms bonded to carbon atoms are in a percentage of from 50 atom% to 100 atom% based on the whole silicon atoms contained in the non-monocrystalline layer.

In a preferred embodiment, in the foregoing light-receiving member, the non-monocrystalline layer further comprises non-monocrystals in which silicon atoms bonded to nitrogen atoms are in a percentage of from 5 atom% to 40 atom% based on the whole silicon atoms contained in the non-monocrystalline layer.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a diagrammatic cross section to illustrate an example of the layer structure of the electrophotographic light-receiving member of the present invention.

Fig. 2 is a diagrammatic side-cutaway view to show an example of an apparatus for producing electrophotographic photosensitive drums by microwave discharging which forms a light-receiving layer of the electrophotographic light-receiving member according to the present invention.

Fig. 3 is a diagrammatic plane-cutaway view of the apparatus shown in Fig. 2.

Fig. 4 illustrates a diagrammatic construction to show an example of an apparatus for producing an electrophotographic photosensitive drum by high-frequency discharging which forms a light-receiving layer of the electrophotographic light-receiving member according to the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The electrophotographic light-receiving member of the present invention can solve all the problems previously discussed, and exhibits very good electrical, optical and photoconductive properties, image quality, durability and service environmental properties.

The present invention will be specifically described below by giving preferred embodiments.

The present inventors took note of any possibility that some modification of surface layers can solve the problems as previously discussed, and made extensive studies. As a result, they have reached a finding that the object can be achieved by specifying the manner of bonds of silicon atoms in the surface layer formed of a non-monocrystalline material constituted of at least silicon atoms, carbon atoms, nitrogen atoms and hydrogen atoms.

In order to improve durability and environmental properties of light-receiving members, it has been common to incorporate carbon atoms or nitrogen atoms together with silicon atoms. In actual circumstances, however, the surface layers have been hitherto formed without taking account of so far as the state of bonds as done by the present inventors. In this instance, silicon atoms, carbon atoms and nitrogen atoms are not uniformly distributed in a deposited film, where the respective silicon atoms, carbon atoms and nitrogen atoms are partly present in a high concentration or a low concentration in such a state that they are mingled one another in mosaic. Hence, in practice, the number of bonds between each different atoms has been smaller than the values expected from a compositional approach.

For example, in the case of silicon atoms and carbon atoms, they have non-uniform distributions in the deposited film. Hence, an attempt to merely increase the flow rate of the gas containing carbon atoms among starting material gases to increase the carbon content in the deposited film so that the probability at which silicon atoms and carbon atom combine can be increased only brings about an increase in bonds between carbon atoms, and is not so effective for increasing the bonds between silicon atoms and carbon atoms. It has been hitherto difficult that silicon atoms having at least one bond to a carbon atom are controlled to be not less than 30 atom% based on the whole silicon atoms in the surface layer. Moreover, increasing the quantity of carbon atoms in this way may result in deterioration of mechanical strength required for electrophotographic light-receiving members and deterioration of other performances such as sufficiently broad optical band gaps, without no satisfactory solution of the above problems. The same can be said to also apply to the bonds between silicon atoms and nitrogen atoms.

All the credit goes to the present inventors, for taking account of the state of chemical bonds that has not been hitherto taken into account and for having achieved the bonding of a large quantity of carbon atoms and nitrogen atoms to silicon atoms without damaging various physical properties that has been hitherto impossible. More specifically, in the present invention, a material in which the percentage of silicon atoms having at least one bond to a carbon atom and/or that of silicon atoms having at least one bond to a nitrogen atom is/are specified to a value or values very larger than ever is used as a material for the surface layer. Its use has led to the accomplishment of an electrophotographic light-receiving member greatly effective for improving weatherability and environmental properties without damaging mechanical strength and transparency and at the same time preventing toner from fogging.

No detailed mechanism is unclear with regard to the effect of preventing toner from fogging. At present, the inventors presume that an optimum state of bonds between silicon atoms, carbon atoms and nitrogen atoms in the outermost surface can minimize the formation of an attraction force (van der Waals attraction or the like) other than the electrostatic attraction acting between the surface of a light-receiving member and the toner.

In the present invention, it is more effective to incorporate fluorine atoms into the surface layer. More specifically, controlling fluorine content in the surface layer makes it possible to more effectively generate the bonds between silicon atoms, carbon atoms and nitrogen atoms. As a function of the fluorine atoms in the film, it also becomes possible to effectively prevent the bonds between silicon atoms, carbon atoms and nitrogen atoms from breaking because of damage caused by coronas or the like. Thus, the introduction of fluorine atoms brings about a remarkable improvement in the effect of the present invention.

The light-receiving member of the present invention will be described in detail with reference to the accompanying drawings.

The electrophotographic light-receiving member shown in Fig. 1, denoted by reference numeral 100, comprises a support 101 for the light-receiving member, and a light-receiving layer 102 provided thereon. The light-receiving layer 102 is formed of A-Si(H,X), and is comprised of a photoconductive layer 103 having a photoconductivity and a surface layer 104. The surface layer 104 is formed of a non-monocrystalline material constituted of silicon atoms, carbon atoms, nitrogen atoms and hydrogen atoms in which silicon atoms bonded to carbon atoms are in a percentage of from 50 to 100 atom% based on the whole silicon atoms and silicon atoms bonded to nitrogen atoms are in a percentage of from 5 to 40 atom% based on the whole silicon atoms.

In the present invention, it is also effective to further incorporate fluorine atoms into the surface layer. Incorporation of fluorine atoms within the range of from 0 to 15 atom%, and preferably from 0.1 to 10 atom%, makes the present invention more remarkably effective and makes it possible to obtain an electrophotographic light-receiving member with a good durability.

In the present invention, controlling bonds between carbon atoms and nitrogen atoms can make the present invention still more effective. More specifically, when the quantity of carbon atoms having at least one bond to a nitrogen atom is controlled so as to be within the range of from 5 to 50 atom% based on the whole carbon atoms, it becomes possible to more improve durability in an environment of low humidity.

In the present invention, it is also possible to further incorporate oxygen atoms in the surface layer. When oxygen atoms are incorporated, the present invention can be made more remarkably effective by controlling the bonds of oxygen atoms to silicon atoms, to carbon atoms and to nitrogen atoms. More specifically, it becomes possible to more improve the durability in an environment of low humidity when the bonds are so controlled that silicon atoms having at least one bond to an oxygen atom are within the range of from 5 to 50 atom% based on the whole silicon atoms, carbon atoms having at least one bond to an oxygen atom are within the range of from 5 to 50 atom% based on the whole carbon atoms and nitrogen atoms having at least one bond to an oxygen atom are within the range of from 5 to 50 atom% based on the whole nitrogen atoms.

The support used in the present invention may be either conductive or electrically insulating. The conductive support may include those made of, for example, a metal such as Al, Cr, Mo, Au, In, Nb, Te, V, Ti, Pt, Pb or Fe, or an alloy of any of these, as exemplified by stainless steel. It is also possible to use a support comprised of a film or sheet of synthetic resin such as polyester, polyethylene, polycarbonate, cellulose acetate, polypropylene, polyvinyl chloride, polystyrene or polyamide, or an electrically insulating support made of glass or ceramic the surface of which has been subjected to conductive treatment at least on the side on which the light-receiving layer is formed.

The support 101 used in the present invention may have the shape of a cylinder with a smooth surface or uneven surface, or a platelike endless belt. Its thickness may be appropriately so determined that the electrophotographic light-receiving member 100 can be formed as desired. In instances in which the electrophotographic light-receiving member 100 is required to have a flexibility, the support 101 may be made as thin as possible so long as it can well function as a support. In usual instances, however, the support 101 may have a thickness of 10 μm or more in view of its manufacture and handling, mechanical strength or the like.

When images are recorded using coherent light such as laser light, the surface of the support 101 may be made uneven so that any faulty images due to what is called interference fringes appearing in visible images can be canceled.

The uneveness made on the surface of the support 101 can be produced by the known methods as disclosed in U.S. Patents No. 4,650,736, No. 4,696,884 and No. 4,705,733.

As another method for canceling the faulty images due to interference fringes occurring when the coherent light such as laser light is used, the surface of the support 101 may be made uneven by making a plurality of sphere-traced concavities on the surface of the support 101. More specifically, the surface of the support 101 is made more finely uneven than the resolving power required for the electrophotographic light-receiving member 100, and also such uneveness is formed by a plurality of sphere-traced concavities. The uneveness formed by a plurality of sphere-traced concavities on the surface of the support 101 can be produced by the known method as disclosed in U.S. Patent No. 4,735,883.

In the present invention, the photoconductive layer 103 that is formed on the support 101 in order to effectively achieve the object thereof and constitutes part of the light-receiving layer 102 is prepared by a vacuum-deposition film-forming method under conditions appropriately numerically set in accordance with film forming parameters so as to achieve the desired performances.

Stated specifically, it can be formed by various thin-film deposition methods as exemplified by glow discharging method including AC discharge CVD method such as low-frequency CVD method, high-frequency CVD method or microwave CVD method, and DC discharge CVD method; and sputtering method, vacuum metallizing method, ion plating method, light CVD method and heat CVD method. When these thin-film deposition methods are employed, suitable ones are selected according to the conditions for manufacture, the extent of a load on capital investment in equipment, the scale of manufacture and the properties and performances desired on electrophotographic light-receiving members produced. Glow discharging method, sputtering method and ion plating method are preferred in view of their relative easiness to control conditions in the manufacture of electrophotographic light-receiving members having the desired performances. The photoconductive layer may be formed using any of these methods in combination in the same apparatus system.

When, for example, the photoconductive layer 103 is formed by glow discharging method, basically an Si-feeding starting material gas capable of feeding silicon atoms (Si), an H-feeding starting material gas capable of feeding hydrogen atoms (H) and/or an X-feeding starting material gas capable of feeding halogen atoms (X) may be introduced in the desired gaseous state into a reactor whose inside can be evacuated, and glow discharge may be caused to take place in the reactor so that the layer comprised of A-Si(H,X) is formed on a given support 101 previously set at a given position.

In the present invention, the photoconductive layer 103 is required to contain hydrogen atoms and/or halogen atoms. This is because they are essential and indispensable for compensating unbonded arms of silicon atoms to improve layer quality, in particular, to improve photoconductivity and charge retentivity. Hence, the hydrogen atoms or halogen atoms or the total of hydrogen atoms and halogen atoms should preferably be in a content of from 1 to 40 atom%, more preferably from 3 to 35 atom%, and most preferably from 5 to 30 atom%, based on the total of the silicon atoms and the hydrogen atoms and/or halogen atoms.

The material that can serve as the Si-feeding gas used in the present invention may include gaseous or gasifiable silicon hydrides (silanes) such as SiH_4, Si_2H_6, Si_3H_8 and Si_4H_{10}, which can be effectively used. In view of readiness in handling for layer formation and Si-feeding efficiency, the material may preferably include SiH_4 and Si_2H_6. These Si-feeding starting material gases may also be used optionally after their dilution with a gas such as H_2, He, Ar or Ne.

To make it more easy to control the percentage in which the hydrogen atoms are incorporated into the photoconductive layer 103 to be formed, these gases may preferably be mixed with a desired amount of a hydrogen gas or a gas of a silicon compound containing hydrogen atoms, when the layer is formed. Each gas may be mixed not only alone in a single species but also in combination of plural species in a desired mixing ratio, without any problems.

In order to structurally introduce the hydrogen atoms into the photoconductive layer 103, the discharge may also be caused to take place in the reactor concurrently in the presence of, besides the above ones, H_2, or a silicon hydride such as SiH_4, Si_2H_6, Si_3H_8 or Si_4H_{10}, or Si-feeding silicon or silicon compounds.

A material useful as a starting material gas for feeding halogen atoms used in the present invention may preferably include gaseous or gasifiable halogen compounds as exemplified by halogen gases, halides, halogen-containing interhalogen compounds and silane derivatives substituted with a halogen. The material may also include gaseous or gasifiable, halogen-containing silicon hydride compounds constituted of silicon atoms and halogen atoms. Halogen compounds that can be preferably used in the present invention may specifically include fluorine gas (F_2) and interhalogen compounds comprising BrF, ClF, ClF_3, BrF_3, BrF_5, IF_3, IF_7 or the like. Silicon compounds containing halogen atoms, what is called silane derivatives substituted with halogen atoms, may specifically include silicon fluorides such as SiF_4 and Si_2F_6, which are preferable examples.

In order to control the quantity of the hydrogen atoms and/or halogen atoms contained in the photoconductive layer 103, for example, the temperature of the support 101, the quantity of starting materials used to incorporate the hydrogen atoms and/or halogen atoms, the discharge power and so forth may be controlled.

It is also effective to incorporate into the photoconductive layer at least one kind of atoms selected from carbon atoms, germanium atoms, tin atoms, oxygen atoms and nitrogen atoms. At least one kind of the atoms selected from carbon atoms, germanium atoms, tin atoms, oxygen atoms and nitrogen atoms should preferably be in a content of from 0.00001 to 50 atom%, more preferably from 0.01 to 40 atom%, and most preferably from 1 to 30 atom%, based on the total of silicon atoms, carbon atoms, germanium atoms, tin atoms, oxygen atoms and nitrogen atoms. At least one kind of atoms selected from carbon atoms, germanium atoms, tin atoms, oxygen atoms and nitrogen atoms may be evenly distributed in the photoconductive layer, or may be partly non-unformly distributed so as for its content to change in the layer thickness of the photoconductive layer.

In the present invention, the photoconductive layer 103 may preferably contain atoms capable of controlling its conductivity as occasion calls. The atoms capable of controlling the conductivity may be contained in the photoconductive layer 103 in an evenly uniformly distributed state, or may be contained partly in such a state that they are distributed non-uniformly in the layer thickness direction.

The above atoms capable of controlling the conductivity may include what is called impurities, used in the field of semiconductors, and it is possible to use atoms belonging to Group IIIb in the periodic table (hereinafter "Group IIIb atoms") capable of imparting p-type conductivity or atoms belonging to Group Vb in the periodic table (hereinafter "Group Vb atoms") capable of imparting n-type conductivity.

The Group IIIb atoms may specifically include boron (B), aluminum (Al), gallium (Ga), indium (In) and thallium (Tl). In particular, B, Al and Ga are preferred. The Group Vb atoms may specifically include phosphorus (P), arsenic (As), antimony (Sb) and bismuth (Bi). In particular, P and As are preferred.

The atoms capable of controlling the conductivity, contained in the photoconductive layer 103, may be preferably in an amount of from 1×10^{-3} to 5×10^4 atom ppm, more preferably from 1×10^{-2} to 1×10^4 atom ppm, and most preferably from 1×10^{-1} to 5×10^3 atom ppm. In order to structurally introduce the atoms capable of controlling the conductivity, e.g., Group IIIb atoms or Group Vb atoms, a starting material for incorporating Group IIIb atoms or a starting material for introducing Group Vb atoms may be fed, when the layer is formed, into the reactor in a gaseous state together with other gases used to form the photoconductive layer 103. Those which can be used as the starting material for introducing Group IIIb atoms or starting material for introducing Group Vb atoms should be selected from those which are gaseous at normal temperature and normal pressure or at least those which can be readily gasified under conditions for the formation of the photoconductive layer. Such a starting material for incorporating Group IIIb atoms may specifically include, as a material for incorporating boron atoms, boron hydrides such as B_2H_6, B_4H_{10}, B_5H_9, B_5H_{11}, B_6H_{10}, B_6H_{12} and B_6H_{14}, and boron halides such as BF_3, BCl_3 and BBr_3. Besides, the material may also include $AlCl_3$, $GaCl_3$, $Ga(CH_3)_3$, $InCl_3$ and $TlCl_3$.

The material that can be effectively used in the present invention as the starting material for incorporating Group Vb atoms may include, as a material for incorporating phosphorus atoms, phosphorus hydrides such as PH_3 and P_2H_4 and phosphorus halides such as PH_4I, PF_3, PF_5, PCl_3, PCl_5, PBr_3, PBr_5 and PI_3. Besides, the material that can be effectively used as the starting material for incorporating Group Vb atoms may also include AsH_3, AsF_3, $AsCl_3$, $AsBr_3$, AsF_5, SbH_3, SbF_3, SbF_5, $SbCl_3$, $SbCl_5$, BiH_3, $BiCl_3$ and $BiBr_3$.

These starting materials for incorporating the atoms capable of controlling the conductivity may be optionally diluted with a gas such as H_2, He, Ar or Ne when used.

The photoconductive layer 103 of the present invention may also contain at least one element selected from Group Ia, Group IIa, Group IVa, Group VIa, Group VIIa, Group VIII, Group Ib, Group IIb and Group VIb atoms of the periodic table in an amount of approximately from 0.1 to 10,000 atom ppm. Any of these elements may be evenly uniformly distributed in the photoconductive layer 103, or contained partly in such a state that they are evenly contained in the photoconductive layer 103 but are distributed non-uniformly in the layer thickness direction.

The Group Ia atoms may specifically include lithium (Li), sodium (Na) and potassium (K); and the Group IIa atoms, beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr) and barium (Ba).

The Group IVa atoms may specifically include titanium (Ti) and zirconium (Zr); and the Group VIa atoms, chromium (Cr), molybdenum (Mo) and tungsten (W).

The Group VIIa atoms may specifically include manganese (Mn); and the Group VIII atoms, iron (Fe), cobalt (Co) and nickel (Ni).

The Group Ib atoms may specifically include copper (Cu), silver (Ag) and gold (Au); and the Group IIb atoms, zinc (Zn), cadmium (Cd) and mercury (Hg).

The Group VIb atoms may specifically include sulfur (S), selenium (Se) and tellurium (Te).

In the present invention, besides the atoms described above, the photoconductive layer 103 may contain any other atoms so long as they are each in a trace amount (1 atom% or less).

In the present invention, the thickness of the photoconductive layer 103 may be appropriately determined as desired, taking account of achieving the desired electrophotographic performance and in view of economical effect. The layer should preferably be formed in a thickness of from 3 to 120 μm, more preferably from 5 to 100 μm, and most preferably from 10 to 80 μm.

In order to form the photoconductive layer 103 that can achieve the object of the present invention, the temperature of the support 101 and the gas pressure inside the reactor must be appropriately set as desired.

The temperature (Ts) of the support 101 may be appropriately selected from an optimum temperature range in accordance with the layer configuration. In usual instances, the temperature should preferably be in the range of from 20 to 500°C, more preferably from 50 to 480°C, and most preferably from 100 to 450°C.

The gas pressure inside the reactor may also be appropriately selected from an optimum pressure range in accordance with the layer configuration. In usual instances, the pressure may preferably be in the range of from 1×10^{-5} to 100 Torr, preferably from 5×10^{-5} to 30 Torr, and most preferably from 1×10^{-4} to 10 Torr.

In the present invention, preferable numerical values for the support temperature and gas pressure necessary to form the photoconductive layer 103 may be in the ranges defined above. In usual instances, these conditions can not be independently separately determined. Optimum values should be determined on the basis of mutual and systematic relationship so that the light-receiving member having the desired properties can be formed.

In the present invention, the surface layer 104 is further formed on the photoconductive layer 103 formed on the support 101 in the manner as described above. This surface layer 104 has a free surface 105, and is provided so that the object of the present invention can be achieved mainly with regard to performance on moisture resistance, continuous repeated use, electrical breakdown strength, service environmental properties and durability.

In the present invention, the photoconductive layer 103 constituting the light-receiving layer 102 and the amorphous material forming the surface layer 104 each have common constituents, silicon atoms, and hence a chemical stability is well ensured at the interface between layers.

The surface layer 104 is formed of a non-monocrystalline material $A\text{-}(Si_xC_yN_z)_tH_uF_v$ as a main component, constituted of silicon atoms, carbon atoms, nitrogen atoms and hydrogen atoms and/or fluorine atoms.

The surface layer 104 formed of $A\text{-}(Si_xC_yN_z)_tH_uF_v$ (wherein $x+y+z$ is 1 and $t+u+v$ is 1) can be formed by plasma CVD method, sputtering method or the like. No matter what method is used, the reaction must be controlled so that the number of silicon atoms having at least one bond to a carbon atom and that of silicon atoms having at least one bond to a nitrogen atom are in a percentage different from conventional cases.

As methods for controlling the bonds of atoms, there is a method in which starting material gases are selected and a method in which electric fields in plasma are controlled. Use of these methods in combination makes it possible to effectively adjust the manner of bonds.

As a method for controlling the reaction so that the number of silicon atoms having at least one bond to a carbon atom in the surface layer, it is effective especially in the case of microwave discharging method to use, as starting material gases, an alkyl silicide such as tetramethylsilane ($Si(CH_3)_4$) or tetaethylsilane ($Si(C_2H_4)_4$) together with a silicon atom-containing gas such as silane (SiH_4) or silicon tetrafluoride (SiF_4) and/or a carbon atom-containing gas such as methane (CH_4) or carbon tetrafluoride (CF_4). As the carbon atom-containing gas, it is also effective to use a gas having a double bond or triple bond and to previously excite it by light, an electric field or the like together with the silicon atom-containing gas.

As a method for controlling the reaction so that the number of silicon atoms having at least one bond to a nitrogen atom in the surface layer, it is more effective to use, as a starting material gas containing nitrogen atoms, a gas containing halogen atoms together with nitrogen atoms as exemplified by chloroamine (NH_2Cl), fluoroamine (NH_2F) or difluoroamine (NHF_2).

In order to optimize the bonds between silicon atoms, carbon atoms and nitrogen atoms in the present invention, it is also effective to use, as starting material gases, molecules simultaneously containing carbon atoms and nitrogen atoms. It is more effective to do so especially when carbon atoms and nitrogen atoms have double bonds or triple bonds. The starting material gas simultaneously containing carbon atoms and nitrogen atoms may include cyan (C_2N_2), hydrogen cyanide (HCN) and hydrocyanic acid ($H_2C_2N_2$). It is also effective to previously excite any of these starting material gases by light, an electric field or the like before its deposition.

As the method in which electric fields in plasma are controlled as a method for controlling the bonds of atoms, there are an instance in which high-frequency discharging method is used and an instance in which microwave discharging method is used. In the high-frequency discharging method, it is effective to cause glow discharge using an applied voltage with a specific frequency to carry out decomposition. It is also effective to simultaneously apply electric fields with plural frequencies so that the control of discharge and the control of ions can be independently carried out.

In the microwave discharging method, it is effective to apply an electric field (a bias) in plasma in addition to microwaves so that ions can be controlled. The bias may have any frequency ranging from that of DC up to high frequencies. The control of ions can be greatly effective especially when a specific frequency is used. The bias should preferably has a frequency of usually from DC to 500 MHz, preferably from 10 kHz to 200 MHz, and most preferably from 100 kHz to 100 MHz. The bias should preferably be at an output of usually from 10 to 5,000 W, preferably from 20 to 1,000 W, and most preferably from 30 to 500 W, per one support.

In the present invention, in order to incorporate hydrogen atoms and fluorine atoms into the surface layer 104, at lease one of a gas containing hydrogen atoms and a gas containing fluorine atoms is preferably used as a starting material gas. The gas containing hydrogen atoms may include silane (SiH_4), methane (CH_4) and hydrogen (H_2). The gas containing fluorine atoms may include silicon tetrafluoride (SiF_4) and carbon tetrafluoride (CF_4).

In the present invention, when a dilute gas is also used in the formation of the surface layer 104, the dilute gas may preferably be exemplified by hydrogen (H_2), argon (Ar) and helium (He).

In the present invention, the surface layer 104 may also optionally contain atoms capable of controlling its conductivity. The atoms capable of controlling the conductivity may be contained in the surface layer 104 in an evenly uniformly distributed state, or may be contained partly in such a state that they are distributed non-uniformly in the layer thickness direction.

The above atoms capable of controlling the conductivity may include what is called impurities, used in the field of semiconductors, and it is possible to use atoms belonging to Group IIIb in the periodic table (hereinafter "Group IIIb atoms") capable of imparting p-type conductivity or atoms belonging to Group Vb in the periodic table (hereinafter "Group Vb atoms") capable of imparting n-type conductivity.

The Group IIIb atoms may specifically include boron (B), aluminum (Al), gallium (Ga), indium (In) and thallium (Tl). In particular, B, Al and Ga are preferred. The Group Vb atoms may specifically include phosphorus (P), arsenic (As), antimony (Sb) and bismuth (Bi). In particular, P and As are preferred.

Besides, the present invention is similarly effective also when a starting material gas containing oxygen atoms, such as oxygen (O_2), nitrogen monoxide (NO), nitrogen dioxide (NO_2), dinitrogen oxide (N_2O), carbon monoxide (CO) or carbon dioxide (CO_2), or a mixed gas of any of these, is incorporated at the same time when the surface layer 104 is formed.

The surface layer 104 according to the present invention is carefully formed so that the required performances can be imparted as desired. More specifically, from the structural viewpoint, the material constituted of Si, C, N and H and/or F takes the form of from crystal to amorphous depending on the conditions for its formation. From the viewpoint of electric properties, it exhibits the nature of from conductive to semiconductive and up to insulating, and also the nature of from photoconductive to non-photoconductive. Accordingly, in the present invention, the conditions for its formation are severely selected as desired so that an $A-(Si_xC_yN_z)_tH_uF_v)$ having the desired properties as intended can be formed.

For example, in order to provide the surface layer 104 mainly for the purpose of improving its breakdown strength, the A-$(Si_xC_yN_z)_tH_uF_v$ is prepared as a non-monocrystalline material having a remarkable electrical insulating behavior in the service environment.

When the surface layer 104 is provided mainly for the purpose of improving the performance on continuous repeated use and service environmental properties, the A-$(Si_xC_yN_z)_tH_uF_v$ is formed as a non-monocrystalline material having become lower in its degree of the above electrical insulating properties to a certain extent and having a certain sensitivity to the light with which the layer is irradiated.

When the A-$(Si_xC_yN_z)_tH_uF_v$ surface layer 104 is formed on the surface of the photoconductive layer 103, the support temperature in the course of the layer formation is an important factor that influences the structure and properties of the layer formed. In the present invention, when the surface layer is formed, the support temperature should be strictly controlled so that the A-$(Si_xC_yN_z)_tH_uF_v$ having the intended properties can be formed as desired.

As the support temperature in the formation of the surface layer 104, useful for effectively achieving what is intended in the present invention, its optimum range is timely selected in accordance with the process by which the surface layer 104 is formed, and the surface layer 104 is formed at such temperature. In usual instances, the layer should be formed at 50 ° C to 400 ° C, and preferably 100 ° C to 350 ° C. For the formation of the surface layer 104, glow discharging method or sputtering method is advantageously employed because of its relative easiness for delicately controlling the compositional ratio of the atoms constituting the layer or for controlling the layer thickness, compared with other methods. When the surface layer 104 is formed by these layer forming methods, the control of discharge power and gas pressure at the time of the layer formation is one of important factors that influences the properties of the A-$(Si_xC_yN_z)_tH_uF_v$, as in the case of the support temperature described above.

As discharge power conditions under which the A-$(Si_xC_yN_z)_tH_uF_v$ having properties for achieving what is intended in the present invention can be effectively prepared in a good productivity, the discharge power may preferably be set at usually 10 to 5,000 W, and preferably 20 to 2,000 W, per one support. Applied voltage should have a frequency of usually from DC to 10 GHz, preferably from 1 MHz to 5 GHz, and most preferably from 10 MHz to 3 GHz. It is effective to further simultaneously apply plural voltages having frequencies within this range.

The gas pressure inside a deposition chamber should be set at usually 0.001 to 3 Torr, preferably 0.005 to 2 Torr, and most preferably 0.01 to 1 Torr, in approximation.

In the present invention, preferable numerical values for the support temperature and discharge power necessary to form the surface layer 104 may be in the ranges defined above. These factors for layer formation can not be independently separately determined. Optimum values of each factor of layer formation should be determined on the basis of mutual and systematic relationship so that the surface layer 104 formed of the A-$(Si_xC_yN_z)_tH_uF_v$ having the desired properties can be formed.

In the electrophotographic light-receiving member of the present invention, the contents of the silicon atoms, carbon atoms, nitrogen atoms, hydrogen atoms and fluorine atoms in the surface layer 104 are important factors according to which the surface layer 104 that can attain the desired properties for achieving the object of the present invention is formed, as in the case of the conditions under which the surface layer 104 is formed.

More specifically, with reference to the representation A-$(Si_xC_yN_z)_tH_uF_v$ set out above, what can be effective in the present invention should be as follows: x is 0.1 to 0.5, preferably 0.15 to 0.45, and most preferably 0.2 to 0.4; y is 0.3 to 0.7, preferably 0.35 to 0.65, and most preferably 0.4 to 0.6; z is 0.01 to 0.3, preferably 0.05 to 0.25, and most preferably 0.1 to 0.2; t is 0.3 to 0.59, and preferably 0.4 to 0.55; u is 0.41 to 0.7, and preferably 0.45 to 0.6; and v is 0 to 0.15, preferably 0.001 to 0.10, and most preferably 0.006 to 0.04.

In the electrophotographic light-receiving member of the present invention, the hydrogen atoms in the surface layer 104 should be in a content of usually 41 to 70 atom%, and preferably 45 to 60 atom%, and the fluorine atoms should be in a content of usually 0 to 15 atom% by weight, preferably 0.1 to 10 atom%, and most preferably 0.6 to 4 atom%, both based on the total amount of the constituent atoms. The light-receiving member formed to have the hydrogen content and fluorine content within these ranges is well applicable as a product hitherto unavailable and remarkably superior in its practical use.

More specifically, any defects or imperfections (mainly comprised of dangling bonds of silicon atoms or carbon atoms) present inside the surface layer formed of A-$(Si_xC_yN_z)_tH_uF_v$ is know to have ill influences on the properties required for electrophotographic light-receiving members. For example, charge performance may deteriorate because of the injection of charges from the free surface; charge performance may vary because of changes in surface structure in a service environment, e.g., in an environment of high humidity; and the injection of charges into the surface layer on account of the photoconductive layer at the time of corona discharging or irradiation with light may cause a phenomenon of after images during repeated use because of entrapment of charges in the defects inside the surface layer. These can be given as the ill influences.

However, the controlling of the hydrogen content in the surface layer so as to be 41 atom% or more brings about a great decrease in the defects inside the surface layer, so that all the above problems can be solved and dramatical improvements can be achieved in respect of electrical properties and high-speed continuous-use performance compared with conventional cases.

On the other hand, if the hydrogen content in the surface layer is more than 71 atom%, the hardness of the surface layer may become lower, and hence the layer can not endure the repeated use in some instances. Thus, the controlling of hydrogen content in the surface layer within the range set out above is one of very important factors for obtaining much superior electrophotographic performance as desired. The hydrogen content in the surface layer can be controlled according to the flow rate of H_2 gas, the support temperature, the discharge power, the gas pressure and so forth.

The controlling of fluorine content in the surface layer so as to be within the range of 0.1 atom% or more also makes it possible to effectively generate the bonds between silicon atoms and carbon atoms in the surface layer. As a function of the fluorine atoms in the film, it also becomes possible to effectively prevent the bonds between silicon atoms and carbon atoms from breaking because of damage caused by coronas or the like.

On the other hand, if the fluorine content in the surface layer is more than 15 atom%, it becomes almost ineffective to generate the bonds between silicon atoms and carbon atoms in the surface layer and to prevent the bonds between silicon atoms and carbon atoms from breaking because of damage caused by coronas or the like. Moreover, residual potential and image memory may become remarkably seen because the excessive fluorine atoms inhibit the mobility of carriers in the surface layer. Thus, the controlling of fluorine content in the surface layer within the range set out above is one of very important factors for obtaining much superior electrophotographic performance as desired. The fluorine content in the surface layer can be controlled according to the flow rate of fluorine-containing gas such as silicon tetrafluoride, the support temperature, the discharge power, the gas pressure and so forth.

The surface layer 104 of the present invention may also contain at least one element selected from Group Ia, Group IIa, Group IVa, Group VIa, Group VIIa, Group VIII, Group Ib, Group IIb, Group IVb and Group VIb atoms of the periodic table in an amount of approximately from 0.1 to 10,000 atom ppm. Any of these elements may be evenly uniformly distributed in the surface layer 104, or contained partly in such a state that they are evenly contained in the surface layer 104 but are distributed non-uniformly in the layer thickness direction.

The Group Ia atoms may specifically include lithium (Li), sodium (Na) and potassium (K); and the Group IIa atoms, beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr) and barium (Ba).

The Group IVa atoms may specifically include titanium (Ti) and zirconium (Zr); and the Group VIa atoms, chromium (Cr), molybdenum (Mo) and tungsten (W).

The Group VIIa atoms may specifically include manganese (Mn); and the Group VIII atoms, iron (Fe), cobalt (Co) and nickel (Ni).

The Group Ib atoms may specifically include copper (Cu), silver (Ag) and gold (Au); and the Group IIb atoms, zinc (Zn), cadmium (Cd) and mercury (Hg).

The Group IVb atoms may specifically include germanium (Ge), tin (Sn) and lead (Pb); and the Group VIb atoms, sulfur (S), selenium (Se) and tellurium (Te).

In the present invention, besides the atoms described above, the surface layer 104 may contain any other atoms so long as they are each in a trace amount (1 atom% or less).

In the present invention, how silicon atoms are bonded in the surface layer concerns a very important constituent factor. In order for the present invention to be effective, the silicon atoms having at least one bond to a carbon atom should preferably be in a percentage of from 50% to 100%, more preferably from 60% to 100%, and most preferably from 70% to 100%, based on the whole silicon atoms in the surface layer; and the silicon atoms having at least one bond to a nitrogen atom, from 5% to 40%, and most preferably from 10% to 30%, based on the whole silicon atoms in the surface layer.

If the composition and the state of bonds in the surface layer are outside the above ranges, any difficulties may arise in respect of strength, transparency, durability, weatherability and so forth and at the same time the present invention may become greatly less effective.

The range of numerical values defining the thickness of layers in the present invention is one of important factors for effectively achieving the object of the present invention.

The range of numerical values defining the thickness of the surface layer 104 in the present invention is appropriately determined as desired according to expected directions so that the object of the present invention can be effectively achieved.

The layer thickness of the surface layer 104 may be appropriately determined as desired on the basis of systematic relationship according to the properties required in each layer region, also in relation to the layer thickness of the photoconductive layer 103. Economical merits including productivity or mass productivity should still also be taken into account.

In the present invention, the surface layer 104 should have a layer thickness of usually from 20 Å to 10 µm, preferably from 100 Å to 5 µm, and most preferably from 500 Å to 2 µm. That is, if the layer thickness is smaller than 20 Å, the present invention can not be well effective, so that the surface layer may be lost because of abrasion or the like during use of the light-receiving member. If the layer thickness is larger than 10 µm, electrophotographic performance may be lowered, e.g., residual potential may increase.

The light-receiving layer of the electrophotographic light-receiving member 100 in the present invention may have a layer thickness appropriately determined as desired in accordance with what is intended.

In the present invention, the light-receiving layer 102 may have a layer thickness appropriately determined as desired in layer thickness relation to the photoconductive layer 103 and surface layer 104 so that the properties imparted to the photoconductive layer 103 and surface layer 104 that constitute the light-receiving layer 102 can be each effectively utilized and the object of the present invention can be effectively achieved. Its thickness may preferably be determined so that the photoconductive layer 103 may have a layer thickness preferably several to several thousand times, and more preferably several tens to several hundred times, the layer thickness of the surface layer 104.

The light-receiving layer 102 should have a layer thickness, as specific numerical values, of usually from 3 to 150 µm, preferably from 5 to 100 µm, and most preferably from 10 to 80 µm.

In the present invention, a blocking layer (a lower surface layer) formed of a non-monocrystalline SiC-(H,X) or the like decreased in the content of nitrogen atoms or containing none of them may be additionally provided between the photoconductive layer and the surface layer characteristic of the present invention. This is also effective for more improving performances such as charge performance.

Between the surface layer 104 and the photoconductive layer 103 of the present invention, there may also be provided with a region in which the content of carbon atoms and/or nitrogen atoms changes in the manner that it decreases toward the photoconductive layer 103. This makes it possible to more decrease the influence of interference due to reflected light at the interface between the surface layer and the photoconductive layer.

In the light-receiving member of the present invention, the light-receiving layer 102 should preferably have on its side of the support 101 a layer region in which aluminum atoms, silicon atoms, hydrogen atoms and/or halogen atoms are contained in such a state that they are distributed non-uniformly in the layer thickness direction.

In the electrophotographic light-receiving member of the present invention, a bonding layer formed of, e.g., Si_3N_4, SiO_2, SiO or a non-monocrystalline material containing at least one of hydrogen atoms and halogen atoms, at least one of nitrogen atoms and oxygen atoms, and silicon atoms may be further provided between the support 101 and the photoconductive layer 103 for the purpose of more improving adhesion. A charge blocking layer may also be provided for the purpose of blocking any injection of charges from the support. A light-absorbing layer may be further provided to prevent interference of light.

A method for producing a photoconductive member formed by plasma-assisted CVD will be described below.

Figs. 2 and 3 illustrate an example of an apparatus for producing the electrophotographic light-receiving member of the present invention by plasma CVD method, using a cylindrical support. Fig. 2 is a diagrammatic cross section of the production apparatus as viewed from its side, and Fig. 3 is a diagrammatic cross section of the apparatus as viewed from its top. In the drawings, reference numeral 201 denotes a reactor, which forms a vacuum airtight structure. Reference numeral 202 denotes a microwave guide dielectric window formed of a material (e.g., quartz glass, alumina ceramics, etc.) capable of transmitting microwave power to the inside of the reactor 201 and keep the vacuum airtightness. Reference numeral 203 denotes a waveguide through which microwave power is transmitted, and is comprised of a rectangular portion extending from a microwave power source to the vicinity of the reactor and a cylindrical portion inserted into the reactor. The waveguide 203 is connected to the microwave power source (not shown) together with a stub tuner (not shown) and an isolator (not shown). The dielectric window 202 is hermetically sealed to the inner wall of the cylindrical portion of the waveguide 203 so that the atmosphere inside the reactor can be maintained. Reference numeral 204 denotes an exhaust tube that opens to the reactor 201 at its one end and communicates with an exhaust system at its the other end. Reference numeral 206 denotes a discharge space surrounded by supports 205.

A bias electrode 211 is an electrode for applying a voltage to the discharge space, and is electrically connected to bias power sources 213 and 214 via a switch 212. The voltage applied to the bias electrode 211 is so designed that it can be supplied from either power source by operating the switch 212.

Using such an apparatus for producing electrophotographic light-receiving members, the electrophotographic light-receiving members are produced in the following way.

First, the reactor 201 is evacuated through the exhaust tube 204 by means of a vacuum pump (not shown) to adjust the pressure inside the reactor 201 to 1×10^{-7} Torr or less. Subsequently, each support 205 is heated by means of a heater 207 to keep its temperature at a given temperature. Then, starting material gases for the photoconductive layer are fed into the reactor via a gas feeding means (not shown). More specifically, starting material gases such as silane gas as a starting material gas for A-Si(H,X), diborane gas as a doping gas and helium gas as a dilute gas are fed into the reactor 201. At the same time, microwaves with a frequency of 2.45 GHz are generated from a microwave power source (not shown), which are passed through the waveguide 203 and introduced into the reactor 201 through the dielectric window 202.

A voltage is further applied to the bias electrode 211 in the discharge space 206, in opposition to the supports 205. Thus, in the discharge space 206 surrounded by the supports 205, the starting material gases are excited by the energy of the microwaves to undergo dissociation, where the electric field formed between the bias electrode 211 and the supports 205 gives constant ion bombardment onto the supports 205, in the course of which the photoconductive layer is formed on the surface of each support 205. At this time, a rotating shaft around which each support 205 is set is rotated by means of a motor 210 to rotate the support 205 about an axis in the generatrix direction of the support, so that a deposited film layer is uniformly formed over the whole periphery of each support 205.

To form the surface layer on the photoconductive layer thus formed, the starting material gases are compositionally made different from those used when the photoconductive layer is formed. For example, silane gas, methane gas, ammonia gas, tetramethylsilane gas, cyan gas, hydrogen gas and silicon tetrafluoride gas optionally together with a dilute gas such as helium gas are fed into the reactor 201, and discharging is initiated in the same manner as in the formation of the photoconductive layer. Thus the surface layer can be formed.

The content of carbon atoms in the surface layer can be controlled by appropriately changing, for example, the ratio of flow rate of silane gas to that of methane gas fed into the discharge space; and the content of nitrogen atoms, by appropriately changing, for example, the ratio of flow rate of silane gas to that of ammonia gas fed into the discharge space.

The manner in which silicon atoms are bonded can be controlled by changing starting material gases methane gas and ammonia gas for tetramethylsilane gas and cyan gas. The voltage and frequency of the bias applied to the discharge space are changed by adjusting the bias electrodes 213 and 214 and operating the switch 212, so that the control can be made more effectively.

The content of hydrogen atoms and the content of fluorine atoms in the surface layer can be controlled as desired, by appropriately changing, for example, the flow rates of hydrogen gas and silicon tetrafluoride gas fed into the discharge space.

EXAMPLES

The the present invention will be more specifically described below by giving Examples.

Example 1

Using the production apparatus as shown in Fig. 2, a light-receiving layer was formed on each mirror-finished aluminum cylinder (the support) to obtain an electrophotographic light-receiving member. At this time, the photoconductive layer and the surface layer were prepared under conditions as shown in Table 1.

Using the apparatus shown in Fig. 2, each member obtained by forming only the surface layer on a cylinder of the same type was separately prepared. Regarding the electrophotographic light-receiving member (hereinafter "drum"), it was set on an electrophotographic copying machine (NP6150, manufactured by Canon Inc., modified for present tests), and electrophotographic performances such as charge performance, sensitivity, fogging in low-humidity environment (atmospheric temperature: 15 °C; humidity: 15%), residual potential, ghost and faulty images at the initial stage were evaluated under various conditions.

Next, the drum was tested on 200,000 sheet running, using a drum heater and in an environment of low humidity of 15 °C atmospheric temperature and 15% relative humidity to make the same evaluation as that at the initial stage. The content and state of bonds of atoms in the surface layer were analyzed by Auger electron spectroscopy, SIMS, ESCA or XMA as occasion calls.

Regarding the member having only the surface layer (hereinafter "sample"), its portions corresponding to image areas were cut out in plural films. Quantitative analysis and analysis of the state of bonds of silicon atoms, carbon atoms, nitrogen atoms, hydrogen atoms and fluorine atoms in the cut films were made by Auger electron spectroscopy, SIMS, RBS, PRD, FT-IR, ESCA, XMA, laser Ramman microanalysis or the heat melting method as occasion calls, and percentages of silicon atoms, carbon atoms, nitrogen atoms, hydrogen atoms, fluorine atoms, silicon atoms with Si-C bonds and silicon atoms with Si-N bonds in the films were each calculated.

The results of the evaluation and the values of the initial quantitative analysis are shown in Tables 2 and 3, respectively.

Comparative Example 1

Drums and samples were prepared using the same apparatus and in the same manner as in Example 1 except that the layers were formed under conditions changed as shown in Table 4. Evaluation and analysis were also made in the same way. Results obtained are shown in Tables 5 and 6, respectively.

Comparison of the data in Tables 2 and 5 makes it clear that the electrophotographic light-receiving member according to the present invention is markedly superior to the light-receiving member outside the present invention, in the environment of low humidity.

Example 2

While the silicon atoms, carbon atoms, nitrogen atoms, hydrogen atoms and fluorine atoms in the surface layer were kept in substantially the same contents as those in the surface layer formed in Example 1, plural kinds of drums 201 to 204 and corresponding samples for analysis were prepared in the same manner as in Example 1 except that the surface layer was formed under conditions changed as shown in Table 7 so that the percentage of silicon atoms having at least one bond to a carbon atom was varied. Evaluation and analysis were made on these drums and samples to obtain the results as shown in Table 8.

From these results it has been ascertained that the light-receiving members of the present invention are remarkably effective on the performance after running especially in the environment of low humidity when the silicon atoms having at least one bond to a carbon atom are in a percentage of at least 50% based on the whole silicon atoms in the surface layer.

Example 3

While the silicon atoms, carbon atoms, nitrogen atoms, hydrogen atoms and fluorine atoms in the surface layer were kept in substantially the same contents as those in the surface layer formed in Example 1, plural kinds of drums 301 to 306 and corresponding samples for analysis were prepared in the same manner as in Example 1 except that the surface layer was formed under conditions changed as shown in Table 9 so that the percentage of silicon atoms having at least one bond to a nitrogen atom was varied. Evaluation and analysis were made on these drums and samples to obtain the results as shown in Table 10.

From these results it has been ascertained that the light-receiving members of the present invention are remarkably effective on the performance after running especially in the environment of low humidity when the silicon atoms having at least one bond to a nitrogen atom are in a percentage of from 10 to 30% based on the whole silicon atoms in the surface layer.

Example 4

While the percentage of silicon atoms having at least one bond to a carbon atom, based on the whole silicon atoms, and the percentage of silicon atoms having at least one bond to a nitrogen atom, based on the whole silicon atoms, were kept in substantially the same ones as those in the surface layer formed in Example 1, plural kinds of drums and corresponding samples for analysis were prepared in the same manner as in Example 1 except that the surface layer was formed under conditions changed so that the percentages of silicon atoms, carbon atoms, nitrogen atoms, hydrogen atoms and fluorine atoms were varied.

Evaluation was made on these drums and samples. As a result, the drums of the present invention proved the present invention to be remarkably effective and showed good electrophotographic performances also in the environment of low humidity when the surface layer had composition represented by A-($Si_xC_yN_z$)tHuFv (wherein $x+y+z$ is 1 and $t+u+v$ is 1) and $0.1 \leqq x \leqq 0.5$, $0.3 \leqq y \leqq 0.7$, $0.01 \leqq z \leqq 0.3$, $0.3 \leqq t \leqq 0.59$ and $0.41 \leqq u \leqq 0.7$.

Example 5

While the contents of silicon atoms, nitrogen atoms and hydrogen atoms and the percentage of silicon atoms having at least one bond to a nitrogen atom, based on the whole silicon atoms in the surface layer, were kept in substantially the same ones as those in the surface layer formed in Example 1, the surface layer was formed under conditions changed so that the content of fluorine atoms was varied. More specifically, samples for analysis were prepared in the same manner as in Example 1 except that the silane gas and/or methane gas used as starting material gas when the surface layer was formed was/were replaced by silicon tetrafluoride gas and/or carbon tetrafluoride gas. These samples were each set on an electrophotographic copying machine (NP6150, manufactured by Canon Inc., modified for present tests), and corona discharging was carried out in a quantity corresponding to 1,000,000 sheet copying under conditions where a voltage of 6 kV was applied to a charge assembly, to compare the number of silicon atoms having at least one bond to a nitrogen atom before or after the corona discharging. Results thus obtained are shown in Table 11.

The results of evaluation as shown in Table 11 show how the silicon atoms having at least one bond to a nitrogen atom changed after the corona charging when compared with those before the corona charging. In the table, letter symbols indicate the following.

AA: Almost no change.
A: Slightly decreased.
B: Considerably decreased, but a change causing no difficulties in practical use when used under usual conditions.
C: Greatly decreased.

From these results it has been ascertained that the light-receiving members of the present invention are markedly superior on the durability against corona charging.

Example 6

Drums were prepared in the same manner as in Example 1 except that the light-receiving layer was formed under conditions changed as shown in Table 12. Values of quantitative analysis made on the drums are shown in Table 13. The same evaluation as in Example 1 was made on the drums. As a result, better results were obtained on durability to ascertain that the present invention was remarkably effective.

Example 7

Drums were prepared in the same manner as in Example 6 except that the light-receiving layer was formed under conditions changed as shown in Table 14. The same evaluation as in Example 1 was made on the drums. As a result, the same good results as those in Example 6 were obtained.

Example 8

Using a deposited film forming apparatus of a high-frequency process type as shown in Fig. 4, a photoconductive layer and a surface layer were formed in the following way under conditions as shown in Table 15.

In Fig. 4, reference numeral 401 denotes a reactor, having a wall 402 serving also as the cathode, a top plate 403, a base plate 404 and insulators 405 and 406 of which a vacuum airtight structure is made up.

A support 407 is set at the middle of the reactor, and serves also as the anode.

To the wall (the cathode) 402, a first high-frequency power source 410 and a second high-frequency power source 411 each having a different oscillation frequency are electrically connected via a matching box 408 and a switch 409. The high-frequency power sources used can be selected by the switch 409 as occasion calls.

Using such an apparatus for producing an electrophotographic light-receiving member, the electrophotographic light-receiving member is produced in the following way.

First, a starting material gas feed valve 412 is closed and an exhaust valve 413 is opened, where the reactor 401 is evacuated through an exhaust tube 414 by means of a vacuum pump (not shown). Its internal pressure is adjusted to about 5 × 10^{-6} Torr or less, reading a vacuum gauge 415.

Subsequently, the support 407 is heated by means of a heater 416 to keep its temperature at a given temperature. Then, starting material gases for the photoconductive layer are fed into the reactor via a starting material gas feeding means 417.

More specifically, starting material gases such as silane gas as a starting material gas for A-Si(H,X), diborane gas as a doping gas and helium gas as a dilute gas are fed into the reactor 401. After making sure that the surface temperature of the support 407 has been set at a given temperature by means of the heater 416, the first high-frequency power source 410 is set on the desired power to cause glow discharge inside the reactor 401.

Thus, in the discharge space 418 surrounded by the wall 402 and the support 407, the starting material gases are excited by the energy of the high-frequency power to undergo dissociation, and the photoconductive layer is formed on the surface of the support 407.

To form the surface layer on the photoconductive layer thus formed, the starting material gases are compositionally made different from those used when the photoconductive layer is formed. For example, silane gas, methane gas, ammonia gas, tetramethylsilane gas, cyan gas, hydrogen gas and silicon tetrafluoride gas optionally together with a dilute gas such as helium gas are fed into the reactor 401, and discharging is initiated in the same manner as in the formation of the photoconductive layer. Thus the surface layer can be formed.

The content of carbon atoms in the surface layer can be controlled by appropriately changing, for example, the ratio of flow rate of silane gas to that of methane gas fed into the discharge space; and the content of nitrogen atoms, by appropriately changing, for example, the ratio of flow rate of silane gas to that of ammonia gas fed into the discharge space. The manner in which silicon atoms are bonded can be controlled by operating the switch 409 to change frequency of the high-frequency power source used and by changing starting material gases methane gas and ammonia gas for tetramethylsilane gas and cyan gas. The content of hydrogen atoms and the content of fluorine atoms in the surface layer can be controlled as desired, by appropriately changing, for example, the flow rates of hydrogen gas and silicon tetrafluoride gas fed into the discharge space.

A drum was produced in this way. Thereafter, using the apparatus shown in Fig. 4, a member (a sample) obtained by forming only the surface layer on a cylinder of the same type was separately prepared.

Analysis on these drum and sample was made in the same manner as in Example 1 to obtain the results as shown in Table 16. Evaluation on the drum was also made in the same manner as in Example 1. As a result, the same good results as those in Example 6 were obtained. From these results it has been ascertained that, without regard to the manner of production, the electrophotographic light-receiving member in which the percentage of silicon atoms having at least one bond to a carbon atom and the percentage of silicon atoms having at least one bond to a nitrogen atom are within the ranges of the present invention is markedly superior to the electrophotographic light-receiving member in which they are outside the rages of the present invention.

Table 1

Film-forming conditions	Layer structure	
	Photoconductive layer	Surface layer
Gas flow rate:		
SiH_4	400 sccm	30 sccm
$Si(CH_3)_4$	0 sccm	80 sccm
CH_4	0 sccm	15 sccm
C_2N_2	0 sccm	15 sccm
NH_3	0 sccm	15 sccm
B_2H_6	60 ppm	0 ppm
H_2	500 sccm	500 sccm
NO	4 sccm	0 sccm
Pressure:	9 mTorr	10 mTorr
Microwave power:	900 W	900 W
Bias power:	500 W	500 W
Bias frequency:	DC	13.56 MHz
Layer thickness:	25 µm	0.1 µm

Table 2

Initial characteristics	
Charge performance:	AA
Sensitivity:	AA
Fog:	AA
Residual potential:	AA
Ghost:	AA
Faulty image:	AA
After running in low-humidity environment	
Charge performance:	AA
Sensitivity:	AA
Fog:	AA
Residual potential:	AA
Ghost:	AA
Faulty image:	AA
Overall evaluation:	AA
AA: Very good A: Good B: No difficulty in practical use C: Sometimes problematic in practical use	

Table 3

Elements	Compositional ratio (at.%)
Si (total)	13.4
Si (Si-C)	12.3
Si (Si-N)	3.4
C (total)	25.3
N (total)	6.0
H	55.3
F	0
Compositional ratio: The total of silicon atoms, carbon atoms, nitrogen atoms, hydrogen atoms and fluorine atoms is regarded as 100 atom%. Si (Si-C): Compositional ratio of Si atoms having Si-C bond. Si (Si-N): Compositional ratio of Si atoms having Si-N bond.	

Table 4

Film-forming conditions	Layer structure	
	Photoconductive layer	Surface layer
Gas flow rate:		
SiH_4	400 sccm	70 sccm
CH_4	0 sccm	300 sccm
B_2H_6	60 ppm	0 ppm
H_2	500 sccm	500 sccm
NO	4 sccm	0 sccm
Pressure:	9 mtorr	10 mtorr
Microwave power:	900 W	900 W
Bias power:	500 W	500 W
Bias frequency:	DC	DC
Layer thickness:	25 µm	0.1 µm

Table 5

Initial characteristics	
Charge performance:	AA
Sensitivity:	A
Fog:	B
Residual potential:	A
Ghost:	A
Faulty image:	AA
After running in low-humidity environment	
Charge performance:	A
Sensitivity:	B
Fog:	C
Residual potential:	C
Ghost:	B
Faulty image:	A
Overall evaluation:	C
AA: Very good A: Good B: No difficulty in practical use C: Sometimes problematic in practical use	

Table 6

Elements	Compositional ratio (at.%)
Si (total)	12.8
Si (Si-C)	3.8
Si (Si-N)	0
C (total)	28.4
N (total)	0
H	58.8
F	0
Compositional ratio: The total of silicon atoms, carbon atoms, nitrogen atoms, hydrogen atoms and fluorine atoms is regarded as 100 atom%. Si (Si-C): Compositional ratio of Si atoms having Si-C bond. Si (Si-N): Compositional ratio of Si atoms having Si-N bond.	

Table 7

Film-forming conditions	Sample No.			
Gas flow rate: (sccm)	201	202	203	204
SiH_4	35	40	50	60
$Si(CH_3)_4$	70	60	40	20
CH_4	45	75	135	195
C_2N_2	15	15	15	15
NH_3	15	15	15	15
H_2	500	500	500	500
Pressure: (mTorr)	10.1	10.0	10.2	10.0
Microwave power: (W)	900	900	900	900
Bias power: (W)	500	500	500	500
Bias frequency: (MHz)	13.56	13.56	13.56	13.56
Layer thickness: (μm)	0.1	0.1	0.1	0.1

Table 8

	201	202	203	204
Si (Si-C) ratio:	0.72	0.62	0.53	0.47
Initial characteristics				
Charge performance:	AA	AA	AA	AA
Sensitivity:	AA	AA	A	A
Fog:	AA	AA	AA	A
Residual potential:	AA	AA	AA	A
Ghost:	AA	AA	AA	A
Faulty image:	AA	AA	AA	AA
After running in low-humidity environment				
Charge performance:	AA	AA	A	A
Sensitivity:	AA	AA	A	A
Fog:	AA	A	B	C
Residual potential:	AA	A	B	B
Ghost:	AA	AA	A	B
Faulty image:	AA	A	A	A
Overall evaluation:	AA	A	B	C

Si (Si-C) ratio: Si(Si-C)/Si(total)

AA: Very good

A: Good

B: No difficulty in practical use

C: Sometimes problematic in practical use

Table 9

Film-forming conditions	Sample No.					
	301	302	303	304	305	306
Gas flow rate: (sccm)						
SiH_4	30	30	30	30	30	30
$Si(CH_3)_4$	80	80	80	80	80	80
CH_4	0	5	10	20	25	30
C_2N_2	30	25	20	10	5	0
NH_3	0	5	10	20	25	30
H_2	500	500	500	500	500	500
Pressure: (mTorr)	10.1	10.0	10.2	10.1	10.9	10.9
Microwave power: (W)	900	900	900	900	900	900
Bias power: (W)	500	500	500	500	500	500
Bias frequency: (MHz)	13.56	13.56	13.56	13.56	13.56	13.56
Layer thickness (μm)	0.1	0.1	0.1	0.1	0.1	0.1

Table 10

	301	302	303	304	305	306
Si (Si-N) ratio:	0.42	0.38	0.27	0.11	0.06	0.04
Initial characteristics						
Charge performance:	A	AA	AA	AA	AA	AA
Sensitivity:	A	AA	AA	AA	AA	A
Fog:	A	AA	AA	AA	AA	A
Residual potential:	B	A	AA	AA	AA	A
Ghost:	A	A	AA	AA	A	A
Faulty image:	A	A	AA	AA	A	A
After running in low-humidity enviroment						
Charge performance:	B	A	AA	AA	A	A
Sensitivity:	A	A	AA	AA	A	A
Fog:	C	B	AA	AA	B	C
Residual potential:	C	B	AA	AA	B	B
Ghost:	B	A	AA	AA	A	B
Faulty image:	A	A	AA	AA	A	A
Overall evaluation:	C	B	AA	AA	B	C

Si (Si-N) ratio: Si(Si-N)/Si(total)
AA: Very good
A: Good
B: No difficulty in practical use
C: Sometimes problematic in practical use

Table 11

	Sample No.						
	401	402	403	404	405	406	407
F Content (at%): Evaluation:	0 B	0.1 A	0.6 AA	3.8 AA	9.5 A	15 B	17 C
F content: The total of silicon atoms, carbon atoms, nitrogen atoms, hydrogen atoms and fluorine atoms is regarded as 100 atom%.							

Table 12

Film-forming conditions	Layer structure		
	Charge blocking layer	Photoconductive layer	Surface layer
Gas flow rate:			
SiH_4	350 sccm	350 sccm	20 sccm
$Si(CH_3)_4$	0 sccm	0 sccm	80 sccm
CH_4	35 sccm	0 sccm	15 sccm
C_2N_2	0 sccm	0 sccm	15 sccm
NH_3	0 sccm	0 sccm	15 sccm
B_2H_6	1,000 ppm	0 ppm	0 ppm
H_2	500 sccm	500 sccm	500 sccm
SiF_4	0 sccm	0 sccm	15 sccm
Pressure:	9 mTorr	10 mTorr	10 mTorr
Microwave power:	900 W	900 W	900 W
Bias power:	500 W	500 W	500 W
Bias frequency:	DC	DC	13.56 MHz
Layer thickness:	3 µm	25 µm	0.3 µm

Table 13

Elements	Compositional ratio (at.%)
Si (total)	13.2
Si (Si-C)	12.1
Si (Si-N)	3.3
C (total)	25.2
N (total)	5.8
H	53.7
F	2.1
Compositional ratio: The total of silicon atoms, carbon atoms, nitrogen atoms, hydrogen atoms and fluorine atoms is regarded as 100 atom%. Si (Si-C): Compositional ratio of Si atoms having Si-C bond. Si (Si-N): Compositional ratio of Si atoms having Si-N bond.	

Table 14

Film-forming conditions	Layer structure		
	Charge blocking layer	Photoconductive layer	Surface layer
Gas flow rate:			
SiH_4	350 sccm	350 sccm	350 sccm
CH_4	35 sccm	35 sccm	0 sccm
$Si(CH_3)_4$	0 sccm	0 sccm	0 sccm
NH_3	0 sccm	0 sccm	0 sccm
C_2N_2	0 sccm	0 sccm	0 sccm
He	500 sccm	500 sccm	500 sccm
B_2H_6	1,000 ppm	0 ppm	0 ppm
SiF_4	0 sccm	0 sccm	0 sccm
Pressure:	11 mTorr	11 mTorr	10 mTorr
Microwave power:	1,000 W	1,000 W	1,000 W
Bias power:	500 W	500 W	500 W
Bias frequency:	DC	DC	DC
Layer thickness:	3 µm	20 µm	5 µm

Table 15

Film-forming conditions	Layer structure		
	Charge blocking layer	Photoconductive layer	Surface layer
Gas flow rate:			
SiH_4	250 sccm	350 sccm	0 sccm
$Si(CH_3)_4$	0 sccm	0 sccm	200 sccm
C_2N_2	0 sccm	0 sccm	10 sccm
He	250 sccm	350 sccm	500 sccm
NO	10 sccm	0 sccm	0 sccm
B_2H_6	1,000 ppm	1 ppm	0 ppm
SiF_4	0 sccm	0 sccm	5 sccm
Pressure:	0.3 Torr	0.5 Torr	0.4 Torr
High-frequency power:	300 W	400 W	500 W
High-frequency:	13.56 MHz	13.56 MHz	70.68 MHz
Layer thickness:	4 µm	20 µm	5 µm

Table 16

Elements	Compositional ratio (at.%)
Si (total)	14.2
Si (Si-C)	12.3
Si (Si-N)	4.0
C (total)	27.1
N (total)	4.8
H	52.6
F	1.3

Compositional ratio:

The total of silicon atoms, carbon atoms, nitrogen atoms, hydrogen atoms and fluorine atoms is regarded as 100 atom%.

Si (Si-C):

Compositional ratio of Si atoms having Si-C bond.

Si (Si-N):

Compositional ratio of Si atoms having Si-N bond.

As described above, the present invention has made it possible to obtain an electrophotographic light-receiving member having a superior durability and a high image quality. The electrophotographic light-receiving member according to the present invention causes less changes in electrophotographic performance on its surface under corona charging especially in an environment of low humidity and proves to be markedly superior to conventional electrophotographic light-receiving members in respect of fog preventive effect and so forth.

To provide an electrophotographic light-receiving member having a good initial-stage electrophotographic performance and also having a good durability especially in an environment of low humidity, the light-receiving member comprises a support 101, a photoconductive layer 103 formed on the support and formed of a non-monocrystalline material mainly composed of silicon atoms, and a surface layer 104 formed of a non-monocrystalline material constituted of silicon atoms, carbon atoms, nitrogen atoms and hydrogen atoms in which silicon atoms having at least one bond to a carbon atom are in a percentage of at least 50 atom% based on the whole silicon atoms in the surface layer.

Claims

1. An electrophotographic light-receiving member comprising a support, a photoconductive layer showing a photoconductivity, formed on the support and formed of a non-monocrystalline material mainly composed of a silicon atom and containing at least one of a hydrogen atom and a halogen atom, and a non-monocrystalline layer formed as a surface layer at the outermost surface, containing at least a silicon atom, a carbon atom, a nitrogen atom and a hydrogen atom, wherein;

   the surface layer contains silicon atoms bonded to carbon atoms, in a percentage of from 50 atom% to 100 atom% based on the whole silicon atoms in the surface layer.

2. The electrophotographic light-receiving member according to claim 1, wherein the surface layer further contains silicon atoms bonded to nitrogen atoms, in a percentage of from 5 atom% to 40 atom% based on the whole silicon atoms in the surface layer.

3. The electrophotographic light-receiving member according to claim 1, wherein the surface layer contains hydrogen atoms in a percentage of from 41 atom% to 70 atom% based on the whole elements in the surface layer.

4. The electrophotographic light-receiving member according to claim 1, wherein the surface layer further contains fluorine atoms.

5. The electrophotographic light-receiving member according to claim 2, wherein the surface layer further contains fluorine atoms.

6. The electrophotographic light-receiving member according to claim 3, wherein the surface layer further contains fluorine atoms.

7. The electrophotographic light-receiving member according to claim 4, wherein the fluorine atoms in the surface layer are in a content of from 0.1 atom% to 10 atom% based on the whole elements in the surface layer.

8. The electrophotographic light-receiving member according to claim 5, wherein the fluorine atoms in the surface layer are in a content of from 0.1 atom% to 10 atom% based on the whole elements in the surface layer.

9. The electrophotographic light-receiving member according to claim 6, wherein the fluorine atoms in the surface layer are in a content of from 0.1 atom% to 10 atom% based on the whole elements in the surface layer.

10. The electrophotographic light-receiving member according to claim 2, wherein the surface layer contains hydrogen atoms in a percentage of from 41 atom% to 70 atom% based on the whole elements in the surface layer.

FIG. 1

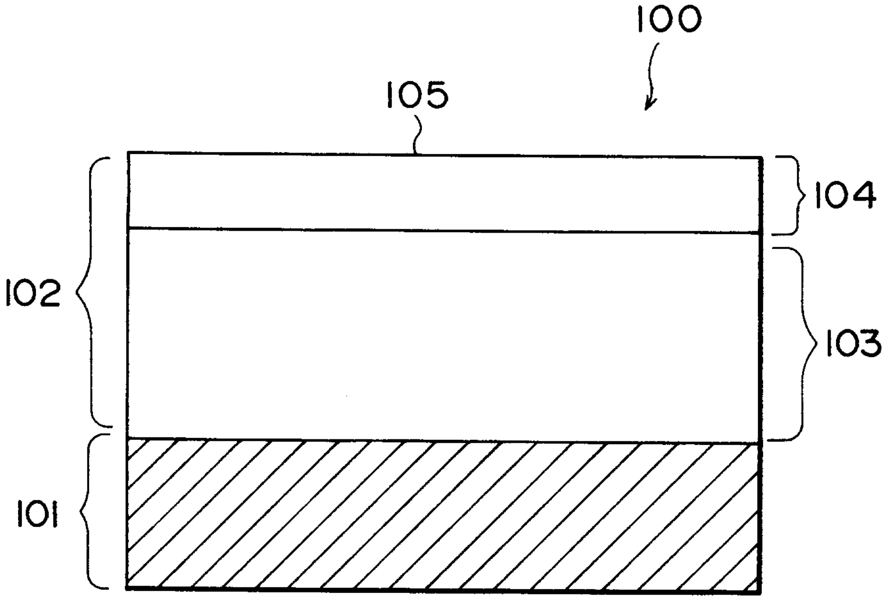


FIG. 2

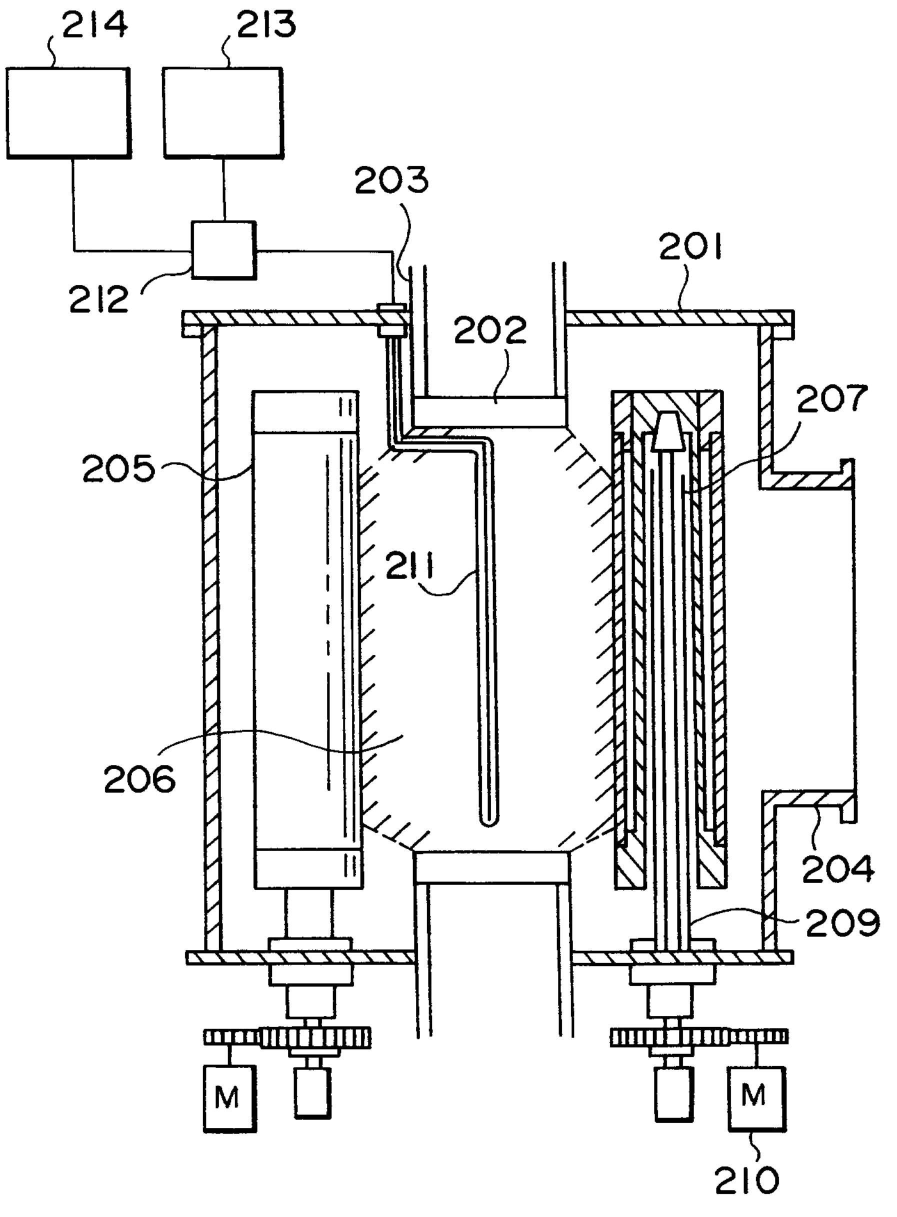


FIG. 3

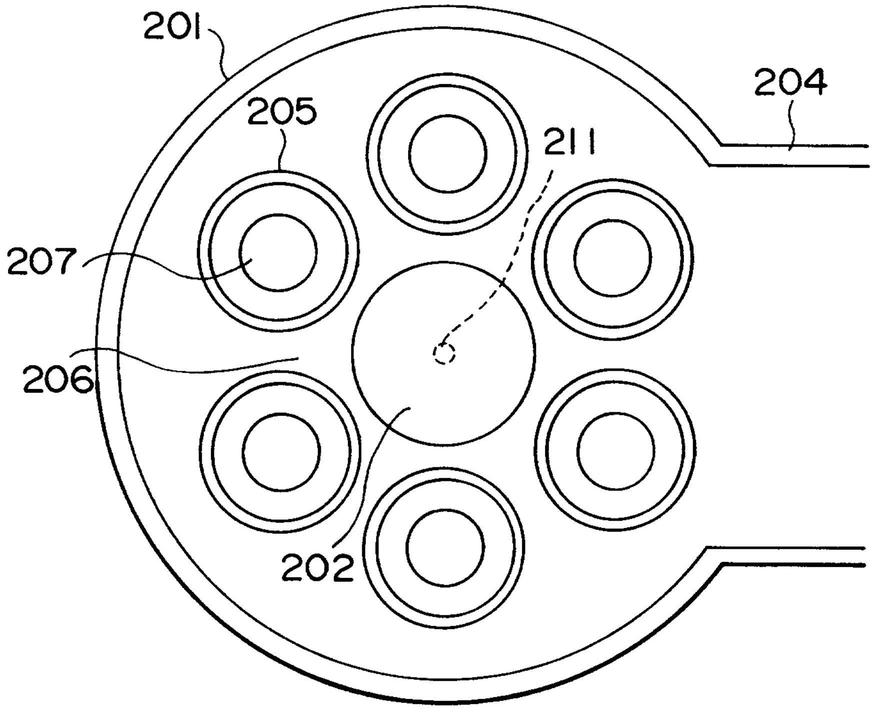
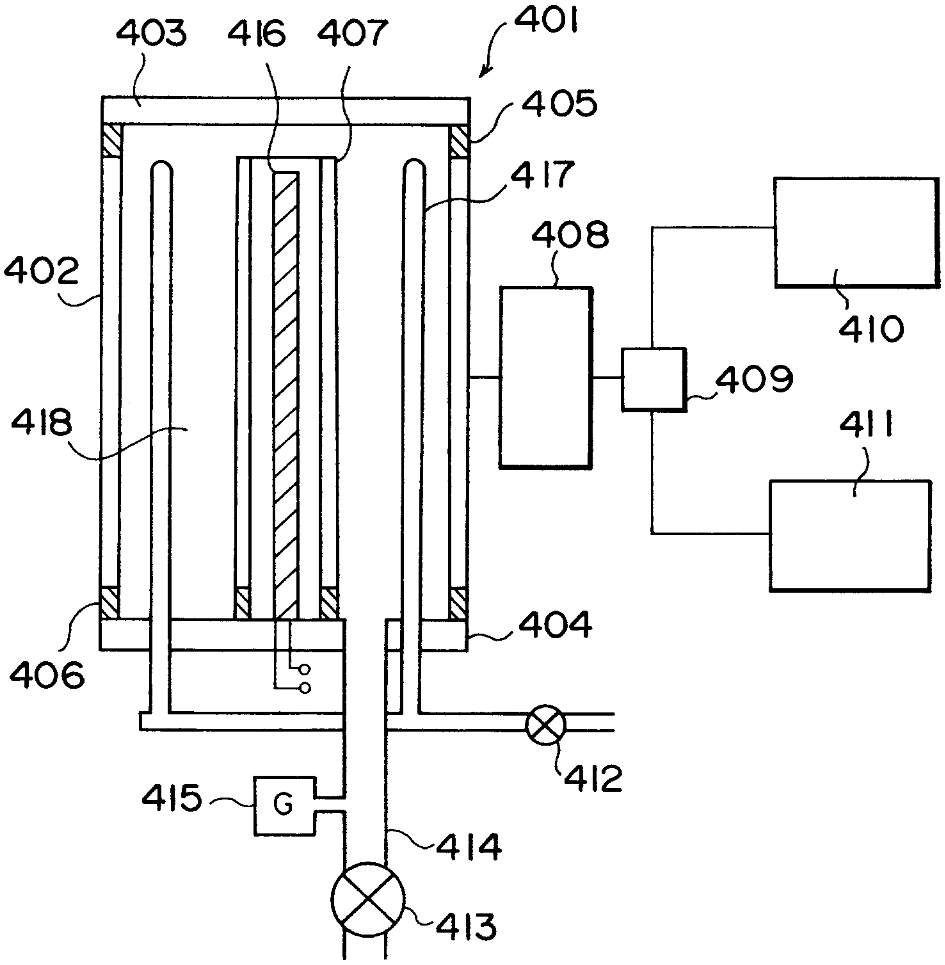


FIG. 4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