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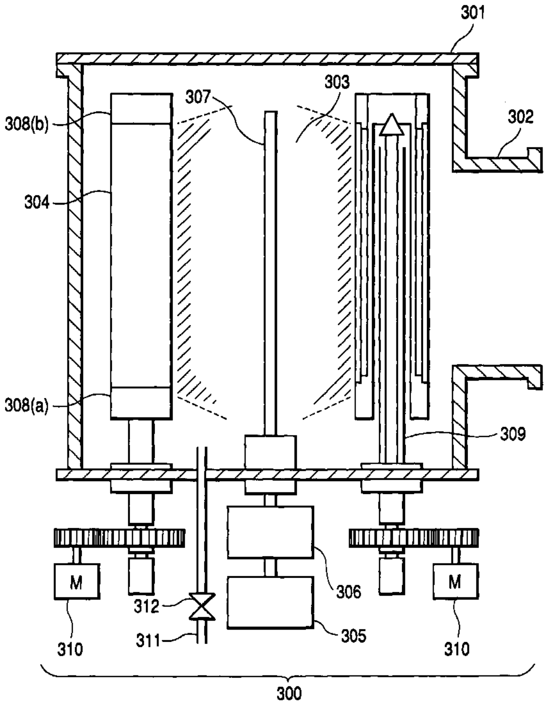
(54) Photosensitive member, process for its production, image forming apparatus having the photosensitive member, and image forming process

(57) In order to improve release properties and slipperiness of toner on a surface of a photosensitive member, the surface layer of the photosensitive member is formed of a non-single-crystal carbon film having a low spin density and a short spin relaxation time and containing at least hydrogen atom, to thereby provide a photosensitive member that can form highly minute and high-grade images and has a superior durability and provide a photosensitive member that has a high sensitivity, may not cause any faulty images due to a leak, and can stably obtain ghost-free, high-grade images without causing any changes with time.

FIG. 3



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Description

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to a photosensitive member, a process for its production, an image forming apparatus having the photosensitive member and an image forming process carried out using the photosensitive member. More particularly, this invention relates, in an electrostatic image forming process including an electrophotographic process, to a photosensitive member as typified by an electrophotographic photosensitive member, that can obtain highly minute images in every environment, may cause no melt-adhesion of toner because of its high release properties even when used in a high-speed process, also has a running performance high enough to maintain such properties, has a high sensitivity, and can stably obtain high-grade images; and a process for its production, an image forming apparatus having such a photosensitive member and an image forming process carried out using the photosensitive member.

Related Background Art

As materials for device members used in photosensitive members for electrostatic image formation including electrophotography, materials such as selenium, cadmium sulfide, zinc oxide, phthalocyanine and amorphous silicon (hereinafter "a-Si") are proposed. Of these, non-single-crystal deposited films containing silicon atoms as a main component, as typified by a-Si, have been proposed as materials for photosensitive members having a high performance and a high durability and free from environmental pollution, as exemplified by amorphous deposited films of a-Si compensated with hydrogen and/or a halogen such as fluorine or chlorine. Some of these have been put into practical use. U.S. Patent No. 4,265,991 discloses a technique concerning an electrophotographic photosensitive member comprising a photoconductive layer mainly formed of a-Si.

Such a-Si type photosensitive members have advantages that they have a high surface hardness, exhibit a high sensitivity to long-wavelength light of semiconductor lasers (770 nm to 800 nm) or the like and also are almost free from deterioration due to repeated use. Hence, they are put into use especially in photosensitive members for electrophotographic apparatus such as high-speed copying machines and LBPs (laser beam printers).

As processes for forming such deposited films, a number of processes are known in the art, as exemplified by sputtering, thermal CVD, photo assisted CVD, and plasma enhanced CVD. In particular, plasma enhanced CVD, i.e., a process in which a source gas is decomposed by glow discharge produced by utilizing a direct current, a high-frequency (RF or VHF) or a microwave to form a deposited film on any desired substrate such as glass, quartz, heat-resistant synthetic film, stainless steel or aluminum is being widely put into practical use in the process for forming amorphous-silicon deposited films used in electrophotography. Apparatus therefor are also proposed in variety.

In recent years, it is also strongly sought to improve film quality and processability, and various measures are studied to do so.

In particular, a plasma enhanced process making use of high-frequency power is widely used because of its various advantages such that it has a high discharge stability and can also be used to form insulating materials such as oxide films and nitride films. In recent years, plasma enhanced CVD carried out using a power source with a high frequency of 50 MHz or above using a diode parallel plate plasma enhanced CVD system, as reported in Plasma Chemistry and Plasma Processing, Vol. 7, No. 3 (1987), pp.267-273, has attracted notice, which shows a possibility of improving the deposition rate without a lowering of the performance of deposited films by making the discharge frequency higher than 13.56 MHz conventionally used. Making the discharge frequency higher in this way is also reported in respect of sputtering, and is widely studied in recent years.

In recent years, because of an increasing demand for high-quality copied images, it is still also strongly sought to provide a technique by which a much higher image quality can be stably provided. Under circumstances where various demands increase on copying machines, e.g., demands for much higher minuteness, higher speed, digital processing, compactness in size, lower cost and so forth, toners are being made to have smaller particle diameters, and it has become popular to use those having a weight-average particle diameter of from 0.005 to 0.008 mm as measured by Coulter Counter or the like. For the achievement of higher speed, such toners with small particle diameter must be improved in their fixing performance, but are disadvantageous for the prevention of their melt-adhesion to photosensitive members that is a conflicting performance. The fact itself that they have small particle diameters is also directed to a disadvantage in respect of melt-adhesion. More specifically, when toners with small particle diameters are removed by cleaning, the contact pressure of a cleaning blade must be changed in order to prevent the toner from escaping. However, since frictional force increases concurrently with high speed processing, it can be said that toners stand tending to cause melt-adhesion.

If the toner has melt-adhered to the drum surface, no latent image is formed because the imagewise exposure light is not transmitted through toner-melt-adhered areas, and such areas appear as minute black spots on images. Also, once the melt-adhesion has occurred, although not appear on copied imaged at the initial stage, the melt-adhesion may grow in the rotational direction with repetition of copying operations to come to cause line faulty images. The melt-adhesion thus grown can only be removed by scraping the photosensitive member surface with alumina powder or the like to remove the melt-adhered toner. This, however, actually means that the photosensitive member must be changed for new one, resulting in a great increase in running cost. Accordingly, it is required to prevent the toner melt-adhesion from occurring and growing.

As techniques to cope with these problems, the following methods are known in the art. First, as a method for making the surface hardly scraped, it is known to form a surface layer using non-single-crystal carbon called a-C (amorphous carbon) or DLC (diamond-like carbon), as disclosed in many publications including, e.g., Japanese Patent Application Laid-open No. 57-114146. As a method for modifying a surface layer, it is also known to change the spin density of surface, as disclosed in, e.g., U.S. Patent No. 4,661,427 and Japanese Patent Application Laid-open No. 61-160754.

However, in the trend toward higher speed and higher minuteness as stated previously, any sufficient attention has not been paid on the release properties or slipperiness of toner on the surface layer. More specifically, in order to cause no toner melt-adhesion, one may contemplate countermeasures such that the surface is modified so as to make the toner hardly adhere to the photosensitive member or the blade is made to have a higher hardness in order to enhance the ability to scrape the toner having adhered. Since, however, frictional force increases and abrasive force increase with an increase in process speed, there is a possibility that the photosensitive member surface is unwantedly scraped even if the surface has been modified to become more effective, unless materials are carefully selected. Also, when the cleaning blade is made to have a higher hardness, its properties come apart from a rubbery state and approach a glassy state, and hence the cleaning blade becomes brittle as the quality of materials, so that there is a possibility that the cleaning blade breaks to cause faulty cleaning. Accordingly, it has now been sought to provide a photosensitive member which has a surface or surface layer having so high a hardness that the photosensitive member surface may not be scraped even under conditions severe on the drum surface as in the high-speed process making use of toners with small particle diameters, and also having been so modified as to cause no toner melt-adhesion, and which may not deteriorate in its function even after copies have been taken over a long period of time and on a large number of sheets.

Under circumstances where various demands increase on copying machines, electrophotographic photosensitive members are also required to have a higher sensitivity, to achieve a higher image quality and to have a thin-film thickness. In such an instance, the surface layer that protects the photosensitive member surface is required to have a low loss and to be formed of a thin film. Accordingly, it has now been sought to provide surface-layer materials that have wide band gaps, have a durability of higher breakdown voltage and can be made into thin films.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a photosensitive member that has solved the above problems, is improved in the release properties and slipperiness of toner on the surface layer (or surface region) so that no melt-adhesion of toner on the photosensitive member surface may occur in every environment and highly minute and high-grade images can be obtained, and has a superior durability.

Another object of the present invention is to provide a photosensitive member that has a high sensitivity, may not cause any faulty images due to a leak, and can stably obtain ghost-free, high-grade images without causing any changes with time.

To achieve the above objects, the present invention provides a photosensitive member comprising a substrate having a conductive surface, and provided thereon a photoconductive region preferably comprising a non-single-crystal material mainly composed of silicon atom, and a surface region provided on the photoconductive region;

the surface region being formed of a non-single-crystal carbon film having a low spin density and a short spin relaxation time and containing at least hydrogen atom.

The present invention also provides an image forming apparatus comprising:

a photosensitive member comprising a conductive substrate, a photoconductive region provided on the substrate and a surface region provided on the photoconductive region; the surface region being formed of a non-single-crystal carbon film having a low spin density and a short spin relaxation time and containing at least hydrogen atom;
a charging device for electrostatically charging the surface of the photosensitive member;
a light source for exposing the surface of the photosensitive member;
a developing device for imparting a toner to the surface of the photosensitive member in accordance with electric charges held on the surface;
a transfer device for transferring the toner imparted to the surface of the photosensitive member; and
a cleaner for cleaning the surface of the photosensitive member.

The present invention still also provides an image forming process comprising the steps of:

electrostatically charging a surface of a photosensitive member comprising a conductive substrate, a photoconductive region provided on the substrate and a surface region provided on the photoconductive region; the surface region being formed of a non-single-crystal carbon film having a low spin density and a short spin relaxation time and containing at least hydrogen atom;
exposing the photosensitive member thus charged;
forming a toner image on the surface of the photosensitive member in accordance with the exposure;
transferring the toner image; and
cleaning the surface of the photosensitive member after the transfer of the toner image.

The present invention further provides a process for producing a photosensitive member, comprising:

applying an energy to an atmosphere containing carbon atom and hydrogen atom in the state of reduced pressure formed in a chamber capable of being evacuated and provided therein with a substrate having thereon a photoconductive region; and

thereby generating plasma to form on the photoconductive region a surface region formed of a non-single-crystal carbon film having a low spin density and a short spin relaxation time and containing at least hydrogen atom.

Thus, in the present invention, the spin density and spin relaxation time in the surface region is taken into account so that the toner can be improved in release properties and slipperiness and the toner can be prevented from melt-adhering to the photosensitive member surface.

Since the toner can be prevented from melt-adhering to the photosensitive member surface, it becomes easy to use toners with smaller particle diameters, so that a photosensitive member that can form more highly minute and high-quality images and also has a high durability can be provided.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1A is a diagrammatic cross-sectional view of a single-layer type photosensitive member according to the present invention, and Fig. 1B a diagrammatic cross-sectional view of a function-separated type photosensitive member according to the present invention.

Fig. 2 is a diagrammatic view for illustrating an example of a deposition system used to form a photosensitive layer on a substrate by PCVD.

Fig. 3 is a diagrammatic view for illustrating an example of a deposition system used to form a photosensitive layer on a substrate by VHF-PCVD.

Fig. 4 is a diagrammatic cross-sectional view of an electrophotographic apparatus as an image forming apparatus of the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The photosensitive member of the present invention has a conductive substrate, a photoconductive region provided on the substrate and a surface region further provided on the photoconductive region. The surface region is formed of a non-single-crystal carbon film having a low spin density and a short spin relaxation time and containing at least hydrogen atoms.

In the photosensitive member of the present invention, the photoconductive region and the surface region may be a photoconductive layer and a surface layer, respectively.

In the photosensitive member of the present invention, the non-single-crystal carbon film may preferably have a spin density of 1×10^{20} spins/cm^3 or below and a spin relaxation time of 10^{-2} seconds or less.

In the photosensitive member of the present invention, the non-single-crystal carbon film may also preferably contain fluorine atoms in the film.

In the photosensitive member of the present invention, the non-single-crystal carbon film may also preferably have fluorine-carbon bonds on its surface or in the vicinity of the surface.

The non-single-crystal carbon film of the photosensitive member of the present invention may preferably be formed using a source gas containing fluorine atoms.

The non-single-crystal carbon film of the photosensitive member of the present invention may preferably be formed by etching carried out in a plasma originating from a source gas containing fluorine atoms.

The photosensitive member of the present invention may preferably be produced using CF_4 gas as the source gas containing fluorine atoms.

In the photosensitive member of the present invention, the surface layer may preferably be formed by decomposing the source gas by plasma enhanced CVD (chemical vapor deposition) employing a high frequency of from 1 to 450 MHz.

In the photosensitive member of the present invention, the surface layer may preferably be formed by decomposing the source gas by plasma enhanced CVD employing a high frequency of from 50 to 450 MHz.

The photosensitive member of the present invention may preferably be provided, between the photoconductive region (layer) and the surface region (layer), an intermediate region (layer) serving as a buffer region (layer), having composition intermediate between the both.

The present invention constituted as described above has been accomplished as a result of the following studies made by the present inventors.

The present inventors prepared several kinds of non-single-crystal carbon films which can be considered to have much higher durability than any conventional surface layer materials, and made extensive studies thereon (herein the non-single-crystal carbon film is mainly meant by a film of amorphous carbon which is neither graphite nor diamond and in the state of a bond intermediate between them, and may be present together with polycrystal or microcrystal).

However, no change was brought about in the frequency of occurrence of melt-adhesion only by making the surface layer have a higher hardness. Then the hardness or contact pressure of the cleaning blade was increased so that the toner can be scraped off once it has melt-adhered, in an attempt to make an improvement in such a direction. Instead, however, it was found that the cleaning blade became greatly damaged to frequently cause faulty cleaning. Namely, it became clear that there is a limit to the prevention of melt-adhesion only by making the surface layer have a higher hardness.

Then, they have made extensive studies in the direction of improving release properties of the surfaces. As a result, they happened to have discovered that there is a correlation between the spin density of surface and the release properties of toner.

Now, using non-single-crystal carbon films having so high a hardness as to be hardly scraped, they made studies on films having a small spin density. As a result, both the release properties and the slipperiness were found to be more improved than those achieved by conventional surface layer materials. However, even when the surface layer has both the properties simultaneously, it was found that these properties could not be maintained in many cases after long-term copying and it was very rare to obtain films that were able to maintain these properties.

In the course of further studies made thereafter, the present inventors have discovered that mere combination of non-single-crystal carbon with low spin density can not be said to be effective, and only a non-single-crystal carbon film having a spin density in a smaller range than a certain specific value and a spin relaxation time shorter than a certain value brings about improvements in release properties and slipperiness, makes such surface layer properties not deteriorate even after long-term copying, and may hardly cause melt-adhesion.

More specifically, it has become possible to improve both the release properties and the slipperiness and also to maintain these properties and make the melt-adhesion hardly occur for the first time when a non-single-crystal carbon film having a higher hardness than conventional materials is used as the surface layer material and the film is so formed as to have a spin density of 1×10^{20} spins/cm^3 or below and a spin relaxation time of 10^{-2} seconds or less.

The reason why the melt-adhesion can be prevented and the intended properties can be maintained when the non-single-crystal carbon film is formed within the scope of the present invention is still unclear, but it is presumed as follows: A non-single-crystal carbon film formed under specific conditions has enabled improvement of copying performances-in initial-stage compared with conventional surface layer materials. Non-single-crystal carbon, when formed under suitable conditions, terminates the surface with hydrogen atoms, so that the film is considered to have so low a surface free energy as to make substances hardly adhere thereto, i.e., to be improved in release properties. It is also known from observation with an atomic force microscope that films smooth on the atomic level can be formed by optimizing film-forming conditions or by making suitable treatment. This is presumed to be the cause of improvement in slipperiness.

However, when dangling bonds are present on the surface in a large number, they act as adsorption centers, on which various matter adsorbs, resulting in an increase in surface free energy to cause damage of release properties. At the same time, adhesion of various matter is considered to also make slipperiness poor. If under such a condition the surface is repeatedly brought into friction with drum peripheral members, the surface atoms begin to come off, so that the dangling bonds are always produced. Under such vicious circle, the toner melt-adheres to particular sites, and once it has melt-adhered thereto, the melt-adhesion grows around there and appears on images, as so presumed.

In the non-single-crystal carbon film, it is difficult to control its spin density compared with conventional a-Si or SiC. Under specific conditions, however, a film can be obtained which has a relatively low spin density for non-single-crystal carbon films, i.e., of about 1×10^{20} spins/cm^3 or below. This enabled more improvement in release properties at the initial stage, but the vicious circle of producing dangling bonds was found to still occur after long-term service. From this fact, it was considered necessary either to decrease the number of the dangling bonds present on the surface at the initial stage or to strengthen the bond to the elements such as hydrogen terminating the surface to restrain the dangling bonds from being produced. There was a limit to decreasing the dangling bonds at the initial stage, but there was room for studies with regard to strengthening the bond to the terminating elements.

When it is intended to strengthen the bonding energy to the terminating elements, this is considered to be conditioned on the presence of less strain in the bond to the surroundings of carbon to which the terminating elements are bonded. If the bonding carbon is bonded to the surroundings under strain, the bonding electrons are considered to become uneven to weaken the bond to the terminating elements. A flicker of bonding electrons that is caused by the bond strain is considered to be observed in wave forms observed by ESR (electron spin resonance absorption), where the spin relaxation time is considered to become shorter as the bond is stabler, and the bond is considered to have less strain as the spin relaxation time is shorter, i.e., a firm bond is established. Thus, it is considered that, if the surface layer can be formed so as to have a surface having a short spin relaxation time, the terminating atoms may not come off and the vicious circle of producing dangling bonds by no means occurs.

In summing up the foregoing, the photosensitive member that may cause no melt-adhesion even after long-term service in a high-speed process is presumed to have been obtained because it has become possible to greatly improve the release properties and slipperiness at the initial stage by using the non-single-crystal carbon and by controlling its spin density to be 1×10^{20} spins/cm^3 or below and also because it has become possible to maintain such properties by controlling its spin relaxation time to be 10^{-2} seconds or less.

When the surface of the non-single-crystal carbon film is terminated with fluorine atoms, the film can have a much lower surface free energy and can be more improved in release properties and slipperiness. Such reinforcement of bonding energy more restrains surface atoms from coming off, and hence can make the melt-adhesion more hardly occur than the termination with elements such as hydrogen atoms.

Termination with fluorine atoms (hereinafter often "fluorination") may be made by a method in which a fluorine-containing gas such as CF_4 is introduced to incorporate fluorine atoms into the film from the beginning of film formation or a method in which the surface is fluorinated with plasma of the fluorine-containing gas after the non-single-crystal carbon film has been formed. In the former method, a soft film may result if fluorine is in a too large proportion in film-forming gases, but the hardness can be maintained so long as the gas ratio is so set as to provide the spin density and spin relaxation time within the scope of the present invention. The reason therefor is unclear, and it is presumed that the hardness can be maintained because the bonding energy has become strong within the scope of the present invention. In the latter method, it is important to take care not to damage the surface by the treatment with fluorine plasma. If the surface is damaged, the surface atoms may instead tend to come off, and hence it is necessary to fluorinate the surface so as to provide the spin density and spin relaxation time within the scope of the present invention.

In addition, as unexpected advantages of the present invention, any lowering of sensitivity that may be caused by the surface layer can be kept minimum, and also a phenomenon of ghost, i.e., a phenomenon in which an image having been copied last remains can be better prevented, and still also an improvement in breakdown voltage has made it possible to form the surface layer in a much smaller layer thickness.

The above three unexpected advantages are presumed as follows:

Measurement of band gaps of the non-single-crystal carbon film in the present invention revealed that the film had greater band gaps than conventional a-C films. This is presumably because the dangling bonds have decreased and also the firm bonds have increased and consequently the bonding energy as the whole film has increased to become the optical band gaps more wide. This wide band gaps makes the loss smaller than in the case of conventional a-C even under the same layer thickness to bring about a more improvement in sensitivity.

With regard to the ghost, it is considered to occur because electric charges are trapped by levels. In the present invention, the levels that trap electric charges are presumed to have been decreased, but this can not be explained only by the levels present in the thin surface layer, which is thousands of angstroms thick at most, and it is considered that some different factor is concerned. However, details are unclear.

In general, in the non-single-crystal carbon film, its active species at the time of formation tend to cover easily the photosensitive member surface, and hence the coverage is improved, whereas, within the scope of the present invention, the denseness is greatly improved in addition to the good coverage. A high denseness is presumed to be attributable to the state of bond, but details are unclear at present. Because of a good coverage, any defects caused by spherical protrusions or the like can be uniformly covered, and also, because of a high denseness, electric charges come to hardly pass through the surroundings of defects, so that the breakdown voltage is improved to make it hard to cause blank areas which may be caused by a leak of electric charges from the surface layer, as so presumed.

The present invention has been accomplished through the studies as stated above.

The present invention will be described below in detail with reference to the accompanying drawings.

Figs. 1A and 1B are diagrammatic cross-sectional views illustrating the layer configuration of electrophotographic photosensitive members according to the present invention. Fig. 1A shows a photosensitive member called a single-layer type, whose photoconductive layer is not functionally separated, and is a photosensitive member has a substrate 101 optionally provided thereon with a-charge injection blocking layer (charge injection blocking region) 102, and superposed thereon a photoconductive layer (photoconductive region) 103 formed of a-Si and containing at least hydrogen atom, and a surface layer (surface region) 104 formed of non-single-crystal carbon, having the characteristics within the scope of the present invention.

Fig. 1B shows a photosensitive member called a function-separated type, whose photoconductive layer is functionally separated into a charge generation layer and a charge transport layer. On a surface of a substrate 101, a charge injection blocking layer 102 is optionally provided, and a photoconductive layer 103 formed of a-Si and containing at least hydrogen atom, which is functionally separated into a charge generation layer 106 and a charge transport layer 105, is deposited thereon. On this layer, a surface layer 104 formed of non-single-crystal carbon, having the characteristics within the scope of the present invention, is superposed. Here, the charge generation layer 106 and the charge transport layer 105 may be used under any positional relationship. Also, when the functional separation is made by a compositional change, the compositional change may be made in a continuous fashion.

In the photosensitive members illustrated in Figs. 1A and 1B, each layer may have a continuous compositional change, or may have no distinctive interface. The charge injection blocking layer 102 may be omitted as occasion calls. For the purpose of, e.g., improving adhesion, an intermediate layer (intermediate region) 104 may also be optionally provided between the photoconductive layer 103 and the surface layer 104 formed of non-single-crystal carbon. The intermediate layer may be formed of a material including SiC, to form a layer having composition intermediate between the photoconductive layer 103 and the surface layer 104, or may also be formed of SiO, SiN or the like. The intermediate layer may also have composition continuously changed.

The non-single-crystal carbon herein referred to chiefly represents amorphous carbon having a nature intermediate between graphite and diamond, and may partly contain microcrystal or polycrystal. Films of these can be formed by plasma enhanced CVD, sputtering, ion implantation or the like. Films formed by plasma enhanced CVD have both a high transparency and a high hardness, and are preferred for their use as surface layers of electrophotographic photosensitive members.

As discharge frequency used in the plasma enhanced CVD when the non-single-crystal carbon film is formed, any frequency may be used. Industrially it is preferable to use a high frequency of from 1 to 450 MHz, in particular, 13.56 MHz, called RF frequency. Especially when a high frequency of from 50 to 450 MHz, called VHF is used, the film can be more improved in both the transparency and the hardness, and is more preferred when used to form the surface layer.

In the case where the non-single-crystal carbon film of the present invention is formed by plasma enhanced CVD, the film can be formed by decomposing a carbon-containing gas by plasma. The carbon-containing gas usable in that instance may include hydrocarbon gases such as CH_4, C_2H_6, C_2H_4 and C_2H_2; gases prepared by bubbling alcohols such as CH_3OH and C_2H_5OH with hydrogen; and halogenated hydrocarbon gases prepared by substituting hydrogen atoms of hydrocarbons such as CH_3F, CH_2F_2 and CH_3Cl with halogen atoms; any of which may be used so long as active carbon radicals can be produced when formed into plasma. Some of these can form films alone, while some must be diluted with hydrogen or dilute gas. Optimum conditions must be selected for each occasion. A mixed gas of any of the above gases may also be used.

Fig. 2 diagrammatically illustrates an example of a deposition system for producing the photosensitive member by plasma enhanced CVD employing a high-frequency power source according to the present invention.

Stated roughly, this system is constituted of a deposition system 2100, a source gas feed system 2200 and an exhaust system (not shown) for evacuating the inside of a reactor 2110. In the reactor 2110 in the deposition system 2100, a cylindrical film-forming substrate 2112 connected to a ground, a heater 2113 for heating the cylindrical film-forming substrate 2112, and a source gas feed pipe 2114 are provided. A high-frequency power source 2120 is also connected to the reactor via a high-frequency matching box 2115.

The source gas feed system 2200 has gas cylinders 2221 to 2226 for source gases and etching gases, such as SiH_4, H_2, CH_4, C_2H_2, NO, B_2H_6 and CF_4, valves 2231 to 2236, 2241 to 2246 and 2251 to 2256, and mass flow controllers 2211 to 2216. The gas cylinders for the respective component gases are connected to the gas feed pipe 2114 in the reactor 2110 through a valve 2260.

As the high-frequency power source used in the present invention, power sources having any output may be used so long as they can generate an output power suited for apparatus used within the range of from 10 W to 5,000 W or above. With regard to the degree of output variability of the high-frequency power source, it may be of any value to obtain the effect of the present invention.

As the high-frequency matching box 2115 used, those having any constitution may preferably be used so long as they can make matching between the high-frequency power source 2120 and load. As methods for the matching, it may preferably be automatically controlled, or may be controlled manually without any adverse effect on the present invention.

As materials for a cathode electrode (inner sidewalls of the reactor) to which the high-frequency power is to be applied, copper, aluminum, gold, silver, platinum, lead, nickel, cobalt, iron, chromium, molybdenum, titanium, stainless steel, and composite materials of two or more of these materials may be used. The cathode electrode may preferably have a cylindrical shape, and may optionally have an oval shape or a polygonal shape. Those having figures similar to the cross-sectional shape of the substrate 2112 are preferred because the distance between the substrate 2112 and the cathode electrode can be kept constant.

The cathode electrode may be optionally provided with a cooling means. As a specific cooling means, the electrode may be cooled with water, air, liquid nitrogen, Peltier devices or the like, which may be selected as occasion calls.

The cylindrical film-forming substrate 2112 may be made of any material and may have any shape in accordance with its uses. For example, with regard to its shape, it may preferably be cylindrical when electrophotographic photosensitive members are produced, or may optionally have the shape of a flat plate or any other shape. With regard to its material, copper, aluminum, gold, silver, platinum, lead, nickel, cobalt, iron, chromium, molybdenum, titanium, stainless steel, and composite materials of two or more of these materials, as well as insulating materials such as polyester, polyethylene, polycarbonate, cellulose acetate, polypropylene, polyvinyl chloride, polyvinylidene chloride, polystyrene, glass, quartz, ceramics and paper which are coated with conductive materials may be used. Of course, these are selected in accordance with film-forming conditions, usage and so forth. Its surface may be shaped by cutting or dimple-working for the purpose of, e.g., preventing interference.

A preferred example of the procedure for the formation of the photosensitive member using the system shown in Fig. 2 will be described below.

The cylindrical film-forming substrate 2112 is set in the reactor 2110, and the inside of the reactor 2110 is evacuated by means of an exhaust device (not shown; e.g., a vacuum pump). Subsequently, the temperature of the cylindrical film-forming substrate 2112 is controlled at a desired temperature within the range of from 20°C to 500°C by means of the heater 2113 for heating the cylindrical film-forming substrate.

Before source gases for forming the photosensitive member are flowed into the reactor 2110, gas cylinder valves 2231 to 2236 and a leak valve 2117 of the reactor are checked to make sure that they are closed, and also flow-in valves 2241 to 2246, flow-out valves 2251 to 2256 and an auxiliary valve 2260 are checked to make sure that they are opened. Then, a main valve 2118 is opened to evacuate the insides of the reactor 2110 and a gas feed pipe 2116.

Next, at the time a vacuum gauge 2119 has been read to indicate a pressure of 5×10^{-6} Torr, the auxiliary valve 2260 and the flow-out valves 2251 to 2256 are closed. Thereafter, gas cylinder valves 2231 to 2236 are opened so that gases are respectively introduced from gas cylinders 2221 to 2226, and each gas is controlled to have a pressure of 2 kg/cm^2 by operating pressure controllers 2261 to 2266. Next, the flow-in valves 2241 to 2246 are slowly opened so that gases are respectively introduced into mass flow controllers 2211 to 2216.

After the film formation is thus ready to start through the above procedure, the photoconductive layer is first formed on the cylindrical film-forming substrate 2112.

More specifically, at the time the cylindrical film-forming substrate 2112 has had a desired temperature, some necessary flow-out valves among the flow-out valves 2251 to 2256 and the auxiliary valve 2260 are slowly opened so that desired source gases are fed into the reactor 2110 from the gas cylinders 2221 to 2226 through a gas feed pipe 2114. Next, the mass flow controllers 2211 to 2216 are operated so that each source gas is adjusted to flow at a desired rate. In that course, the divergence of the main valve 2118 is so adjusted that the pressure inside the reactor 2110 comes to be a desired pressure of not higher than 1 Torr, while watching the vacuum gauge 2119. At the time the internal pressure has become stable, a high-frequency power source 2120 is set at a desired electric power, and a high-frequency power is supplied to the cathode electrode through the high-frequency matching box 2115 to cause high-frequency glow discharge to take place. The source gases fed into the reactor 2110 are decomposed by the discharge energy thus produced, so that a desired deposited layer mainly composed of silicon is formed on the cylindrical film-forming substrate 2112. After a film with a desired thickness has been formed, the supply of high-frequency power is stopped, and the flow-out valves 2251 to 2256 are closed to stop source gases from flowing into the reactor 2110. The formation of the photoconductive layer is thus completed.

When the surface layer is formed on the photoconductive layer, basically the above operation may be repeated, where film-forming gases may be fed to start discharging. Types and mixing ratio of gases used, film-forming pressure, high-frequency power and its frequency, film-forming temperature and so forth must be set at suitable values before the non-single-crystal carbon film contributory to the effect of the present invention can be formed. This, however, does not mean that any special apparatus is required. The film may be formed using any conventional plasma enhanced CVD system.

The mixing ratio of gases may differ depending on gas species and can not absolutely be prescribed. For example, there is a tendency that it is better for unsaturated hydrocarbon gases to be diluted with hydrogen gas and for saturated hydrocarbon gases not to be so much diluted with hydrogen gas. With regard to film-forming pressure, films may be formed at a pressure within the same range as that of conventional film-forming conditions. It may differ depending on gas species and can not absolutely be prescribed. There is a tendency that it is better for the pressure to be set lower to restrain polymerization from taking place in the vapor phase. With regard to high-frequency power, C-H bonds can not be cut off and no radicals can be formed unless a discharge energy highr than a certain level is imparted. If on the other hand a too high discharge energy is imparted, re-liberation and sputtering may occur to undesirably make film-forming rate extremely low. When a coaxial cylindrical film-forming furnace is used, a power of about 2,000 W or below is preferred. With regard to frequency, it is better to use higher frequency to form highly hard and low-loss films with ease, but use of a too high frequency may cause layer thickness distribution. With regard to film-forming temperature, films may be formed at a temperature within the same range as that of conventional film-forming conditions. If films are formed at a too high temperature, a narrow band gap may result to tend to cause an increase in loss, and hence it is preferable not to set temperature so much high.

Thus, the respective preset values are not so much different from those in conventional film-forming conditions. However, it is considered that the spin density and spin relaxation time have so great a dependence on film-forming parameters that it has been hitherto impossible to form precise films in a good reproducibility.

A specific procedure of the film formation is as described below.

Some necessary flow-out valves among the valves 2251 to 2256 and the auxiliary valve 2260 are slowly opened so that source gases, e.g., CH_4 gas and H_2 gas, necessary for the surface layer are fed into the reactor 2110 from the gas cylinders 2221 to 2226 through a gas feed pipe 2114. Next, the mass flow controllers 2211 to 2216 are operated so that each source gas is adjusted to flow at a desired rate. In that course, the divergence of the main valve 2118 is so adjusted that the pressure inside the reactor 2110 comes to be a desired pressure of not higher than 1 Torr, while watching the vacuum gauge 2119. At the time the internal pressure has become stable, a high-frequency power source 2120 is set at a desired electric power, and a high-frequency power is supplied to the cathode electrode through the high-frequency matching box 2115 to cause high-frequency glow discharge to take place. The source gases fed into the reactor 2110 are decomposed by the discharge energy thus produced, so that the surface layer is formed. After a film with a desired thickness has been formed, the supply of high-frequency power is stopped, and the flow-out valves 2251 to 2256 are closed to stop source gases from flowing into the reactor 2110. The formation of the surface layer is thus completed.

In the course of film formation, the cylindrical film-forming substrate 2112 may be rotated at a stated speed by means of a driving system (not shown). When the film is required to have a much higher hardness, a DC bias voltage may further be applied to the high frequency power through a low-pass filter (not shown).

In order to more improve the release properties of the surface layer, its surface may be fluorinated by subjecting it to fluorine treatment or etching with plasma formed by decomposing a gas containing fluorine atoms. When fluorinated by fluorine plasma, the effect of the present invention can be attained so long as the spin density and spin relaxation time as defined in the present invention are satisfied. When fluorinated, types and mixing ratio of gases used, film-forming pressure, high-frequency power and its frequency, processing temperature, processing time and so forth must be set at suitable values. This, however, does not mean that any special apparatus is required. The surface may be treated using any conventional plasma enhanced CVD system.

Stated specifically, usable gases are fluorine-containing gases as exemplified by CF_4, CH_3F, CH_2F_2, CHF_3, C_2F_4, C_2H_3F, ClF_3, SF_6, HF and F_2, and any gases may be used so long as active fluorine radicals can be produced when formed into plasma. These may be diluted with dilute gas when used. As a tendency, in the case of gases having strong ethcing properties, they may preferably be diluted in a large quantity.

With regard to processing pressure, the pressure may be set within the same range as that in conventional film-forming conditions. It may differ depending on gas species, and can not absolutely be prescribed. A too low pressure is not preferable in some cases because the surface roughness tends to increase. With regard to high-frequency power, C-F bonds can not be cut off and no fluorine radicals can be formed unless a discharge energy not lower than a certain level is imparted. On the other hand, it is not preferable to impart a too high discharge energy because etching may proceed to damage the surface to tend to produce dangling bonds. When a coaxial cylindrical film-forming furnace is used, a power of about 2,000 W or below is preferred.

Fig. 3 diagrammatically illustrates a preferred example of an apparatus for producing photosensitive members (electrophotographic photosensitive members) by plasma enhanced CVD according to an embodiment different from that of Fig. 2. This Fig. 3 diagrammatically illustrates a partial cross section of the apparatus at the part of its reactor and the part of its substrate stand which has substrates.

In Fig. 3, reference numeral 300 denotes a deposition system; and 301, a reactor which is so set up that it can be kept in a vacuum atmosphere. Reference numeral 302 denotes an exhaust tube that opens to the inside of a reactor 301 at one end thereof and communicates with an exhaust system (not shown) at the other end thereof. Reference numeral 303 denotes a discharge space surrounded by a plurality of cylindrical film-forming substrates 304. A high-frequency power source 305 is electrically connected to an electrode 307 via a high-frequency matching box 306. The cylindrical film-forming substrates 304 are each provided around a rotating shaft 309 while being set on holders 308(a) and 308(b). These are so set as to be rotatable by means of a motor 310 if necessary.

As a source gas feed system (not shown), the same system as the one shown in Fig. 2 may be used. The component gases are mixed and are fed into the reactor 301 through a gas feed pipe 311 via a valve 312.

As the high-frequency power source used in the present film-forming system, power sources having any output may be used so long as they can generate an output power suited for apparatus used within the range of from 10 W to 5,000 W or above. With regard to the degree of output variability of the high-frequency power source, it may be of any value to obtain the effect of the present invention.

As the high-frequency matching box 306 used, those having any constitution may preferably be used so long as they can make matching between the high-frequency power source 305 and load. As methods for the matching, it may preferably be automatically controlled, or may be controlled manually without any adverse effect on the present invention.

As materials for the electrode 307 to which the high-frequency power is to be applied, copper, aluminum, gold, silver, platinum, lead, nickel, cobalt, iron, chromium, molybdenum, titanium, stainless steel, and composite materials of two or more of these materials may be used. The electrode may preferably have a cylindrical shape, and may optionally have an oval shape or a polygonal shape. The shape may preferably be determined in accordance with the shape of arrangement of the substrates 304.

The electrode 307 may be optionally provided with a cooling means. As a specific cooling means, the electrode may be cooled with water, air, liquid nitrogen, Peltier devices or the like, which may be selected as occasion calls.

The cylindrical film-forming substrates 304 may be made of any material and may have any shape in accordance with its uses, as previously described.

Fig. 4 schematically illustrates the constitution of an apparatus, for describing an example of an image forming process carried out by an electrophotographic apparatus as the image forming apparatus that utilizes electrostatic images. A photosensitive member 401 is rotated in the direction of an arrow X. Around the photosensitive member 401, a primary charging device 402, an electrostatic latent image forming portion 403, a developing device 404, a transfer medium feed system 405, a transfer charging device 406(a), a separation charging device 406(b), a cleaner 407, a transport system 408, a charge elimination light source 409, a transporting guide 419 and so forth are provided.

An example of the image forming process will be more specifically described below. The photosensitive member 401 is uniformly electrostatically charged by means of the primary charging device 402, to which a high voltage is applied. An electrostatic latent image is formed on the photosensitive member at its electrostatic latent image forming portion, i.e., the portion on which light is projected which is emitted from a lamp 410, reflects from an original 412 placed on an original glass plate 411, passes through mirrors 413, 414 and 415 to form an image through a lens 418 of a lens unit 417 and is then guided through a mirror 416. To this latent image, a toner with a negative polarity is fed from the developing device 404 to form a toner image.

Meanwhile, a transfer medium P is passed through the transfer medium feed system 405 and is fed in the direction of the photosensitive member 401 while adjusting its leading-part feed timing by means of resist rollers 422. A positive electric field, having a polarity reverse to that of the toner, is imparted to the transfer medium P on the back thereof at the gap between the transfer charging device 406(a) and the photosensitive member 401. As the result, the negative-polarity toner image formed on the surface of the photosensitive member is transferred to the transfer medium P. Next, optionally utilizing the curvature of the photosensitive member, the transfer medium P is separated from the photosensitive member 401 by means of the separation charging device 406(b) to which a high-voltage AC voltage is applied. The transfer medium P is passed through the transfer medium transport system 408 to reach a fixing device 424, where the toner image is fixed, and the transfer medium P with the fixed image is delivered out of the apparatus.

The toner remaining on the photosensitive member 401 is collected by a magnet roller 427 and a cleaning blade 421 which are provided in a cleaning unit 407, and the remaining electrostatic latent image is erased through means of the charge elimination light source 409. Reference numeral 420 denotes a blank exposure light source provided in order to eliminate charges from part of the surface of the photosensitive member 401 so that the toner may not adhere to an unauthorized area of the photosensitive member 401.

EXAMPLES

The present invention will be further described below by giving Examples. The present invention is by no means limited by these Examples.

(Example 1)

Using the plasma enhanced CVD system shown in Fig. 2, a lower blocking layer and a photoconductive layer were deposited on a cylindrical aluminum substrate under conditions shown in Table 1, and a surface layer was successively formed thereon under conditions shown in Table 2. Here, the flow rate of hydrogen gas and also the high-frequency power were varied to produce five photosensitive members A to E whose surface layers have different spin densities and spin relaxation times. The values of the spin density and spin relaxation time of each film formed were as shown in Table 6.

Table 1

Conditions for Production of Photosensitive Member (lower blocking layer, photoconductive layer) Lower blocking layer	
SiH_4	260 sccm
H_2	500 sccm
NO	7 sccm
B_2H_6	2,100 ppm
Power	110 W
Internal pressure	0.43 torr
Layer thickness	1.5 μm
Photoconductive layer	
SiH_4	510 sccm
H_2	450 sccm
B_2H_6	10 ppm (ratio to SiH_4)
Power	450 W
Internal pressure	0.55 torr
Layer thickness	20 μm

Table 2

Conditions for Formation of Surface Layer (Example 1, Comparative Example 1)	
CH_4	100 sccm
H_2	variable
Power	variable
Frequency	13.56 MHz
Internal pressure	0.4 torr
Layer thickness	0.1 μm

Five drums produced in the manner as described above were mechanically rubbed on their surfaces at a certain strength as a substitute test for a durability test to be made using a copying machine, and thereafter were each mounted on the copying machine so that performances after long-term service were estimated. First, the drum was rotated at a process speed of 400 mm/sec, and a polishing SiC tape (LT-C2000, available from Fuji Photo Film Co., Ltd.) having an average particle diameter (8 μm) substantially equal to that of toners was brought into contact with it, which was then held down with a parallel pin of 3 mm diameter and 20 mm wide at the contact area, thus the drum surface was rubbed under application of a load. Also, the polishing tape was always moved at about 1 mm/sec so that always virgin areas were fed to keep polishing force constant and also no polish tailings gave an adverse effect. Such forced friction was carried out for 80 minutes.

The five drums thus prepared were each mounted on a modified machine of a copying machine NP6062, manufactured by CANON INC. A test chart available from CANON INC. (trade number: FY9-9058) was placed on the glass plate and its copies were taken on 10,000 sheets of A4-size paper under usual amount of exposure. Here, a toner having an average particle diameter of 8 μm was used as the toner, a cleaning blade having a hardness lower by 4 degrees as JIS hardness than usual ones was used as the cleaning blade, and also the blade pressure was set lower than usual so that the copies were taken in an environment tending to cause melt-adhesion. After 10,000 sheet running, images were evaluated on two kinds of images, the image copied from the test chart and an image copied from a halftone chart available from CANON INC. (trade number: FY9-9042). Whether or not melt-adhesion occurred was examined and thereafter the drum was taken out to observe its surface condition by the use of a microscope to examine whether or not any minute melt-adhered matter not appearing on images was present.

Performance test results obtained by the above evaluation are shown in Table 6.

(Comparative Example 1)

Using the plasma enhanced CVD system shown in Fig. 2, a lower blocking layer and a photoconductive layer were deposited on a cylindrical aluminum substrate under conditions shown in Table 1, and then a surface layer was deposited thereon. The surface layer was formed under the same conditions as those shown in Table 2 except that the flow rate of hydrogen gas and the high-frequency power were so varied as to form surface layers having spin densities and spin relaxation times outside the scope of the present invention. Thus, photosensitive members F and G were produced. The values of the spin density and spin relaxation time are shown in Table 6.

Then, the same evaluation as in Example 1 was made on these photosensitive members.

Results of examination on any changes in performances are shown in Table 6 together with the results in Example 1.

In the evaluation on images formed after 10,000 sheet running, black spot-like marks, although very minute, were seen in the photosensitive member F. In the photosensitive member G, horizontal lines caused by faulty cleaning and black lines considered due to melt-adhesion were seen. No influence of melt-adhesion upon images was seen in all instances where the other photosensitive members were used.

Next, the drums were each taken out of the copying machine and observed with a microscope. As a result, no marks of melt-adhesion were seen at all in respect of the photosensitive members A to E, which were within the scope of the present invention, whereas marks of melt-adhesion were seen in respect of the photosensitive members F and G. Especially with regard to the photosensitive member G, marks of its growth in the direction of the drum rotation were seen, which were in agreement with the stains of melt-adhesion appearing on images.

As can be seen from Example 1 and Comparative Example 1, the spin density and the spin relaxation time must be 1×10^{20} spins/cm^3 or below and 10^{-2} seconds or less, respectively.

(Example 2)

Using the plasma enhanced CVD system shown in Fig. 2, a lower blocking layer and a photoconductive layer were deposited on a cylindrical aluminum substrate under conditions shown in Table 1. Then, using the plasma enhanced CVD system shown in Fig. 2, a surface layer was deposited under conditions as shown in Table 3 in which the gas flow rate and the high-frequency power were set at suitable values to incorporate fluorine atoms in the surface layer, thus photosensitive member H was produced. Also, after the surface layer was deposited under conditions shown in Table 2 but setting the flow rate of hydrogen gas and high-frequency power at suitable values, the photosensitive member surface was exposed to fluorine plasma under conditions for fluorination as shown in Table 4 to effect fluorination, thus photosensitive member I was completed. Here, the surface was treated under conditions so selected that the surface layer had the spin density and spin relaxation time within the scope of the present invention. The spin density and the spin relaxation time were as shown in Table 7.

These drums were tested in the same manner as in Example 1 to make the polishing test and the test to make evaluation on whether or not the melt-adhesion occurred in the modified copying machine Next, fluorine quantities before and after the tests were measured to evaluate the retention of fluorine atoms as its proportion to the initial quantity. The fluorine quantity was measured by X-ray photoelectron spectroscopy (XPS) to measure fluorine quantity in the very vicinity of the surface (to about 50 angstrom depth). The results were indicated as the ratio of a value after test to a value of initial stage.

Test results obtained by the above evaluation are shown in Table 7.

(Comparative Example 2)

Using the plasma enhanced CVD system shown in Fig. 2, a lower blocking layer and a photoconductive layer were deposited on a cylindrical aluminum substrate under conditions shown in Table 1. Then, using the plasma enhanced CVD system shown in Fig. 2, a surface layer incorporated with fluorine atoms in the film was formed under conditions as shown in Table 3, thus photosensitive member J was produced. Also, after the surface layer was deposited under conditions shown in Table 2, the photosensitive member surface was exposed to fluorine plasma under conditions for fluorination as shown in Table 4 to effect fluorination, thus photosensitive member K was completed. Here, the surface was treated under conditions so selected that the surface layer had the spin density and spin relaxation time outside the scope of the present invention. The spin density and the spin relaxation time were as shown in Table 7.

Next, the drums thus produced were tested to make evaluation in the same manner as in Example 2.

Test results thus obtained are shown in Table 7 together with the results in Example 2.

In the case where the photosensitive members H and I were used (Example 2), which were within the scope of the present invention, no marks of melt-adhesion were seen at all on both the images and the drums. In the measurement of fluorine quantity, even after the test, the photosensitive members H and I were found to have retained fluorine atoms by about 80% and about 75%, respectively, of the quantity immediately after production.

On the other hand, in the case where the photosensitive members J and K were used (Comparative Example 2), black spots, although minute, considered due to melt-adhesion were seen on images. The melt-adhesion was also seen on the drums. As a result of the measurement of fluorine quantity, the fluorine atoms present immediately after production decreased to about 20% and about 15%, respectively, of the quantity before the test. In this instance, it was considered that the polishing caused the vicious circle that the fluorine atoms on the surface came off to bring about an increase in dangling bonds and the dangling bonds made the frictional force greater, resulting in occurrence of melt-adhesion, although slightly.

As can be seen from Example 2 and Comparative Example 2, even the fluorine atoms introduced in order to improve release properties and slipperiness can maintain the intended effect only when the films were so formed or treated as to control the spin density and spin relaxation time within the scope of the present invention, and can not be effective when they are outside the scope of the present invention.

(Example 3)

Using the plasma enhanced CVD system shown in Fig. 2, a lower blocking layer and a photoconductive layer were successively superposed on a cylindrical aluminum substrate under conditions shown in Table 1. Then, using the plasma enhanced CVD system shown in Fig. 3, a surface layer was formed under conditions as shown in Table 5. Here, as discharge frequencies, three kinds, 50, 100 and 200 MHz, were used, and the flow rate of hydrogen gas and the high-frequency power were set at suitable values to select film-forming conditions so that the spin density and the spin relaxation time were controlled within the scope of the present invention. Thus, photosensitive members L, M and N were produced.

Next, these were tested in the same manner as in Example 1 to make the polishing test and the test to make evaluation on melt-adhesion.

Results obtained are shown in Table 8. As can be seen from this results and Example 1 (discharge frequency: 13.56 MHz), photosensitive members that can obtain the effect of the present invention can be produced without regard to the differences in the high-frequency power oscillation frequency and apparatus used to form surface layers.

Table 3

Conditions for Formation of Surface Layer (Example 2, Comparative Example 2)	
CH_4	100 sccm
CF_4	variable
Power	variable (800-1,200 W)
Frequency	13.56 MHz
Internal pressure	0.3 torr
Layer thickness	0.1 μm

Table 4

Fluorine Plasma Conditions (Example 2, Comparative Example 2)	
CF_4	variable
Power	variable (800-1,200 W)
Frequency	13.56 MHz
Internal pressure	0.6 torr

Table 5

Conditions for Formation of Surface Layer (Example 3)	
CH_4	100 sccm
H_2	variable
Power	variable
Frequency	variable (50, 100, 200MHz)
Internal pressure	2 mTtorr
Layer thickness	0.1 µm

Table 6

Evaluation on Melt-adhesion by Accelerated Test				
	Spin density (spin/cm^3)	Spin relaxation time (sec.)	Influence on images	Microscopic surface observation
Example 1:				
A	8.7E18	5.2E-3	A	A
B	1.5E19	6.8E-3	A	A
C	3.6E19	7.2E-3	A	A
D	5.4E19	8.5E-3	A	A
E	8.9E19	9.2E-3	A	A
Comparative Example 1:				
F	1.8E20	2.6E-2	B	B
G	2.1E20	5.7E-2	C	C

Influence on images:
A: No influence of melt-adhesion.
B: Minute black spots are seen.
C: Line marks of melt-adhesion are seen.
Microscopic surface observation:
A: No melt-adhesion.
B: Minute melt-adhesion is seen.
C: Grown melt-adhesion is seen.

Table 7

Evaluation under Different Conditions for Fluorination					
	Spin density (spin/cm^3)	Spin relaxation time (sec.)	(1)	(2)	Fluorine quantity: Pre-test/post-test ratio
Example 2:					
H	2.7E19	5.5E-3	A	A	80%
I	5.3E19	7.1E-3	A	A	75%
Comparative Example 2:					
J	1.5E20	3.1E-2	B	B	20%
k	3.7E20	4.8E-2	B	C	15%

(1): Influence on images:
A: No influence of melt-adhesion.
B: Minute black spots are seen.
C: Line marks of melt-adhesion are seen.
(2): Microscopic surface observation:
A: No melt-adhesion.
B: Minute melt-adhesion is seen.
C: Grown melt-adhesion is seen.

Table 8

Evaluation under Different High-frequency Power			
	Frequency (MHz)	Influence on images	Microscopic surface observation
Example 3:			
L	50	A	A
M	100	A	A
N	200	A	A
Influence on images: A: No influence of melt-adhesion. B: Minute black spots are seen. C: Line marks of melt-adhesion are seen. Microscopic surface observation: A: No melt-adhesion. B: Minute melt-adhesion is seen. C: Grown melt-adhesion is seen.			

(Example 4)

Using the plasma enhanced CVD system shown in Fig. 2, a lower blocking layer and a photoconductive layer were deposited on a cylindrical aluminum substrate under conditions shown in Table 1, and then a surface layer was deposited thereon. The surface layer was formed under conditions shown in Table 2 but changing the flow rate of hydrogen gas and the high-frequency power so as to form a surface layer under the same conditions as in Example 1 by which a spin density and a spin relaxation time is made within the scope of the present invention. Thus, photosensitive member O was produced.

Next, using a drum exclusive test machine having the same layout as a copying machine, the sensitivity of the drum was measured. The drum was rotated at a process speed of 400 mm/sec, and a corona charging device was operated so as to impart a charge potential of about 400 V to the surface. Thereafter, the amount of light was changed at the exposure position, and surface potential was measured at the development position. Here, the amount of exposure light at the time when the surface potential is 50 V is indicated as the sensitivity. The sensitivity was evaluated in comparison with that of a conventional surface layer.

Next, using the above drum exclusive test machine, changes in surface potential were measured under various conditions. To make evaluation on ghost potential, the drum surface was charged and thereafter halftone potential was imparted after its one round through the same process as a copying process of exposure, charge elimination and so forth, where a difference in potential between exposed areas and unexposed areas was observed to know the value. Judgement was made on whether or not there was a problem in practical use when the difference in potential was calculated as an image.

To examine differeneces in durability of breakdown voltage, using a modified machine of NP6062, the grid of a corona charging device was removed therefrom and charge potential was set a little higher than usual to make up an environment tending to cause leaks. Copies were taken using such a modified machine, and images at the initial stage were compared with images after 1,000 sheet copying, where the number of faulty images which were blank in white (white dots) caused by leaks was counted. With regard to its evaluation, it was indicated as a comparison with the number obtained when a similar test was made on conventional surface layers.

Results thus obtained on the evaluation of sensitivity, evaluation on ghost potential and evaluation on faulty images caused by leaks are shown in Table 9.

(Comparative Example 3)

Using the plasma enhanced CVD system shown in Fig. 2, a lower blocking layer and a photoconductive layer were deposited on a cylindrical aluminum substrate under conditions shown in Table 1, and then a surface layer was deposited thereon. The surface layer was formed under conditions shown in Table 2 but changing the flow rate of hydrogen gas and the high-frequency power so as to form a surface layer under the same conditions as in Comparative Example 1 by which a spin density and a spin relaxation time is made outside the scope of the present invention. Thus, photosensitive member P was produced.

Subsequently, evaluation was made in the same manner as in Example 4.

Results obtained are shown in Table 9 together with the results in Example 4.

Table 9

Evaluation of Sensitivity and Breakdown Strength					
	Spin density (spin/cm^3)	Spin relaxation time (sec.)	Sensitivity *	Ghost *	Breakdown strength *
Example 4:					
O	2.4E19	5.8E-3	AA	AA	AA
Comparative Example 3:					
P	1.6E20	2.4E-2	A	A	A
AA: Very good. A: On the conventional level B: No problem in practical use. C: Problematic in practical use in some cases.					

* compared with the conventional

In Comparative Example 3, the results were equivalent to those of the conventional surface layer formed of SiC. On the other hand, in Example 4, which was within the scope of the present invention, the sensitivity was found to less deteriorate than that of the conventional surface layer. This was an unexpected result, and was presumably because the dangling bonds decreased, and hence atoms contributing to bond increased, resulting in an increase in bonding energy on the whole to make band gaps greater and bring about a decrease in loss in the surface layer.

In the evaluation on ghost potential, Comparative Example 3, which was outside the scope of the present invention, showed the same results as conventional photosensitive members. On the other hand, in Example 4, which was within the scope of the present invention, it was found that the ghost potential was smaller than that of conventional photosensitive members and the phenomenon of ghost hardly occurred. The reason therefor can not be explained with ease only by the surface layer of thousands of angstroms thick at most, and is unclear at present.

In the test of durability of breakdown voltage, Comparative Example 3, which was outside the scope of the present invention, was found to give the same results as conventional photosensitive members. On the other hand, in Example 4, which was within the scope of the present invention, white spots were found to very less occur. As a result of microscopic observation of the surfaces of the drums taken out after the test, in Comparative Example 3, leaks were observed to have occurred at the edges of spherical protrusions, whereas, in Example 4, marks of leaks were little observed around the spherical protrusions. This difference is presumed to be due to a good coverage for the non-single-crystal carbon film within the scope of the present invention and in addition an improved denseness of the film. As the result, the breakdown strength is considered to have been improved.

According to the present invention, as described above, the surface region (layer) is formed of the non-single-crystal carbon film having a low spin density and a short spin relaxation time and containing at least hydrogen atom, so that the release properties and slipperiness of the toner are both improved. Thus, the present invention can realized the photosensitive member that may cause no melt-adhesion of toner on drum surface in every environment and has a superior durability.

The present invention can also realize the photosensitive member that has a high sensitivity, may hardly cause the phenomenon of ghost, may not cause any faulty images due to leaks of surface charge, and can stably obtain high-grade images without causing any changes with time.

In order to improve release properties and slipperiness of toner on a surface of a photosensitive member, the surface layer of the photosensitive member is formed of a non-single-crystal carbon film having a low spin density and a short spin relaxation time and containing at least hydrogen atom, to thereby provide a photosensitive member that can form highly minute and high-grade images and has a superior durability and provide a photosensitive member that has a high sensitivity, may not cause any faulty images due to a leak, and can stably obtain ghost-free, high-grade images without causing any changes with time.

Claims

1. A photosensitive member comprising a conductive substrate, a photoconductive region provided on the substrate and a surface region provided on the photoconductive region;
   the surface region being formed of a non-single-crystal carbon film having a low spin density and a short spin relaxation time and containing at least hydrogen atom.

2. The photosensitive member according to claim 1, wherein the non-single-crystal carbon film has a spin density of 1×10^{20} spins/cm^3 or below and a spin relaxation time of 10^{-2} seconds or less.

3. The photosensitive member according to claim 1 or 2, wherein the non-single-crystal carbon film contains fluorine atom in the film.

4. The photosensitive member according to claim 3, wherein the non-single-crystal carbon film has a fluorine-carbon bond on its surface or in the vicinity of the surface.

5. The photosensitive member according to any one of claims 1 to 4, which further comprises, between the photoconductive region and the surface region, an intermediate region having composition intermediate between the both regions.

6. The photosensitive member according to any one of claims 1 to 5, wherein the photoconductive region and the surface region have a photoconductive layer and a surface layer, respectively.

7. The photosensitive member according to any one of claims 1 to 6, wherein the surface region is formed using a source gas containing fluorine atom.

8. The photosensitive member according to claim 7, wherein the source gas containing fluorine atom comprises CF_4 gas.

9. The photosensitive member according to any one of claims 1 to 8, wherein the surface region is formed by plasma enhanced chemical vapor deposition employing a high frequency of from 1 MHz to 450 MHz.

10. The photosensitive member according to claim 9, wherein the high frequency is in the range of from 50 MHz to 450 MHz.

11. The photosensitive member according to any one of claims 1 to 10, wherein the photoconductive region comprises a non-single-crystal material mainly composed of silicon atom.

12. The photosensitive member according to any one of claims 1 to 11, wherein the non-single-crystal carbon film comprises an amorphous carbon film.

13. An image forming apparatus comprising:

    a photosensitive member comprising a conductive substrate, a photoconductive region provided on the substrate and a surface region provided on the photoconductive region; the surface region being formed of a non-single-crystal carbon film having a low spin density and a short spin relaxation time and containing at least hydrogen atom;
    a charging device for electrostatically charging the surface of the photosensitive member;
    a light source for exposing the surface of the photosensitive member;
    a developing device for imparting a toner to the surface of the photosensitive member in accordance with electric charges held on the surface;
    a transfer device for transferring the toner imparted to the surface of the photosensitive member; and
    a cleaner for cleaning the surface of the photosensitive member.

14. The image forming apparatus according to claim 13, wherein the non-single-crystal carbon film has a spin density of 1×10^{20} spins/cm^3 or below and a spin relaxation time of 10^{-2} seconds or less.

15. The image forming apparatus according to claim 13 or 14, wherein the non-single-crystal carbon film contains flu-

orine atom in the film.

16. The image forming apparatus according to claim 15, wherein the non-single-crystal carbon film has fluorine-carbon bond on its surface or in the vicinity of the surface.

17. The image forming apparatus according to any one of claims 13 to 16, which further comprises, between the photoconductive region and the surface region, an intermediate region having composition intermediate between the both regions.

18. The image forming apparatus according to any one of claims 13 to 17, wherein the photoconductive region and the surface region have a photoconductive layer and a surface layer, respectively.

19. The image forming apparatus according to any one of claims 13 to 18, wherein the surface region is formed using a source gas containing fluorine atom.

20. The image forming apparatus according to claim 19, wherein the source gas containing fluorine atom comprises CF_4 gas.

21. The image forming apparatus according to any one of claims 13 to 20, wherein the surface region is formed by plasma enhanced chemical vapor deposition employing a high frequency of from 1 MHz to 450 MHz.

22. The image forming apparatus according to claim 21, wherein the high frequency is in the range of from 50 MHz to 450 MHz.

23. The image forming apparatus according to any one of claims 13 to 22, wherein the photoconductive region comprises a non-single-crystal material mainly composed of silicon atom.

24. The image forming apparatus according to any one of claims 13 to 23, wherein the non-single-crystal carbon film comprises an amorphous carbon film.

25. The image forming apparatus according to any one of claims 13 to 24, wherein the cleaner has a blade.

26. An image forming process comprising the steps of:

electrostatically charging a surface of a photosensitive member comprising a conductive substrate, a photoconductive region provided on the substrate and a surface region provided on the photoconductive region; the surface region being formed of a non-single-crystal carbon film having a low spin density and a short spin relaxation time and containing at least hydrogen atom;
exposing the photosensitive member thus charged;
forming a toner image on the surface of the photosensitive member in accordance with the exposure;
transferring the toner image; and
cleaning the surface of the photosensitive member after the transfer of the toner image.

27. The image forming process according to claim 26, wherein the non-single-crystal carbon film has a spin density of 1×10^{20} spins/cm^3 or below and a spin relaxation time of 10^{-2} seconds or less.

28. The image forming process according to claim 26 or 27, wherein the non-single-crystal carbon film contains fluorine atom in the film.

29. The image forming process according to claim 28, wherein the non-single-crystal carbon film has fluorine-carbon bond on its surface or in the vicinity of the surface.

30. The image forming process according to any one of claims 26 to 29, which further comprises, between the photoconductive region and the surface region, an intermediate region having composition intermediate between the both regions.

31. The image forming process according to any one of claims 26 to 30, wherein the photoconductive region and the surface region have a photoconductive layer and a surface layer, respectively.

32. The image forming process according to any one of claims 26 to 31, wherein the cleaning is carried out using a blade.

33. The image forming process according to any one of claims 26 to 32, wherein the exposure comprises blank exposure.

34. The image forming process according to any one of claims 26 to 33, wherein the steps are repeated in that order.

35. A process for producing a photosensitive member, comprising:

applying an energy to an atmosphere containing carbon atom and hydrogen atom in the state of reduced pressure formed in a chamber capable of being evacuated and provided therein with a substrate having thereon a photoconductive region; and
thereby generating plasma to form on the photoconductive region a surface region formed of a non-single-crystal carbon film having a low spin density and a short spin relaxation time and containing at least hydrogen atom.

36. The process for producing a photosensitive member according to claim 35, wherein the non-single-crystal carbon film has a spin density of 1×10^{20} spins/cm^3 or below and a spin relaxation time of 10^{-2} seconds or less.

37. The process for producing a photosensitive member according to claim 35 or 36, wherein the atmosphere contains fluorine atom.

38. The process for producing a photosensitive member according to claim 37, wherein the fluorine atom is fed by CF_4 gas.

39. The process for producing a photosensitive member according to any one of claims 35 to 38, wherein the plasma is generated using a high frequency of from 1 MHz to 450 MHz.

40. The process for producing a photosensitive member according to claim 39, wherein the high frequency is in the range of from 50 MHz to 450 MHz.

FIG. 1A

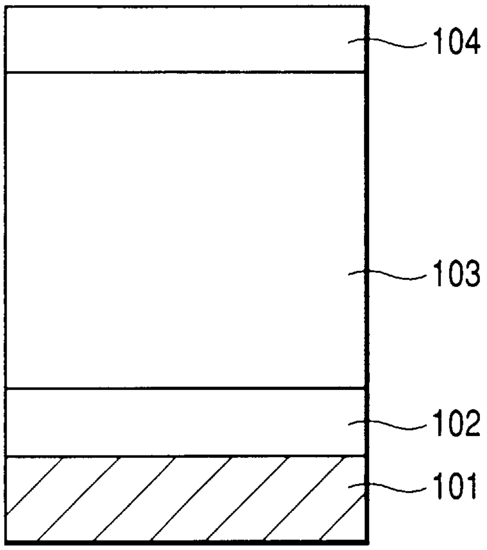

FIG. 1B

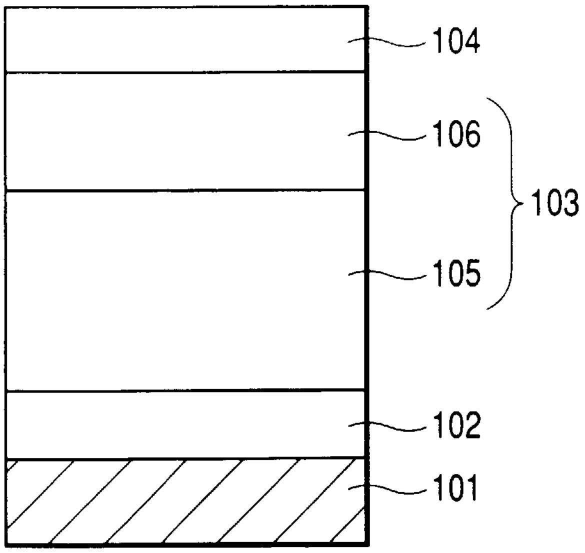

FIG. 2

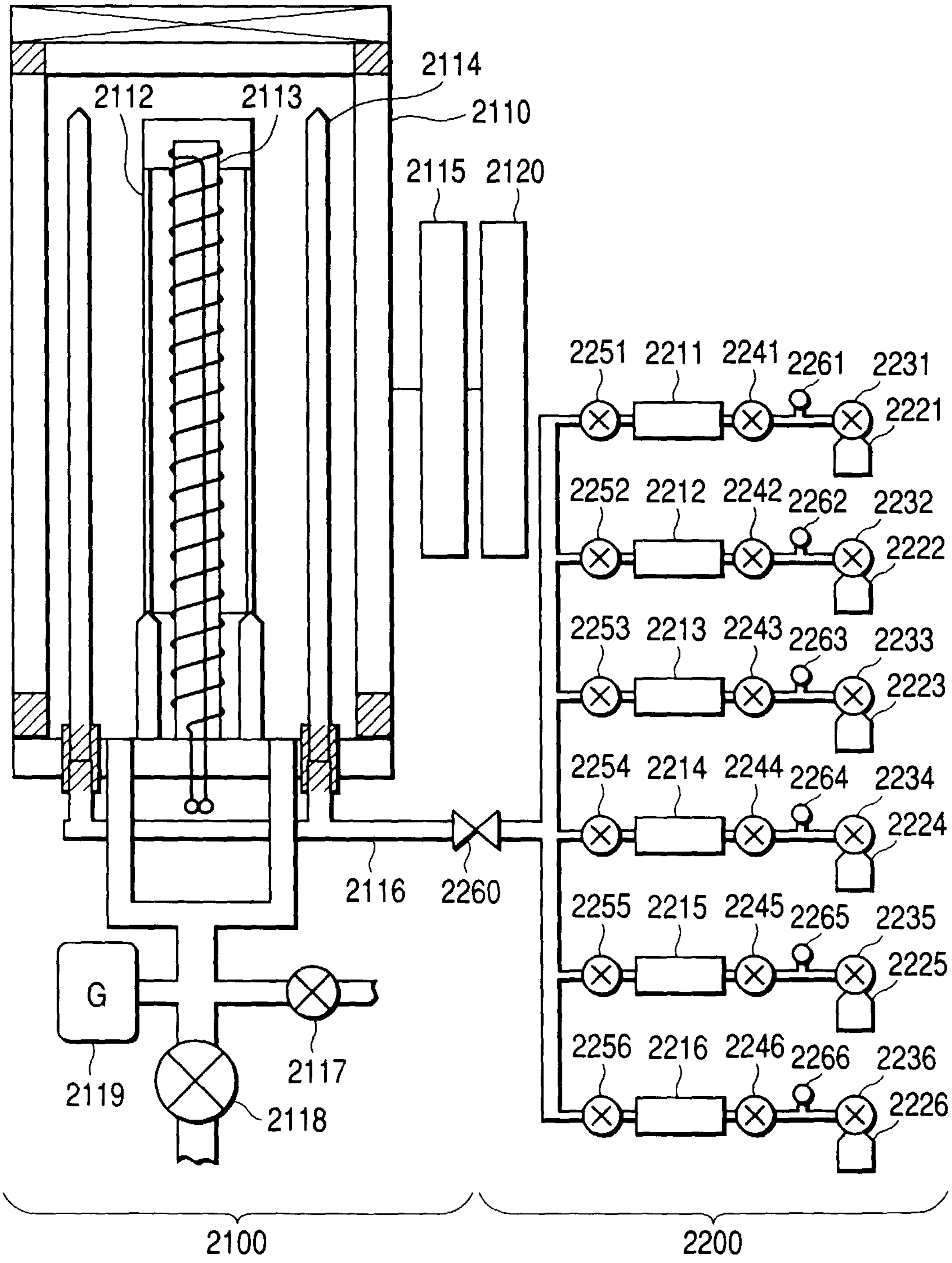
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FIG. 3

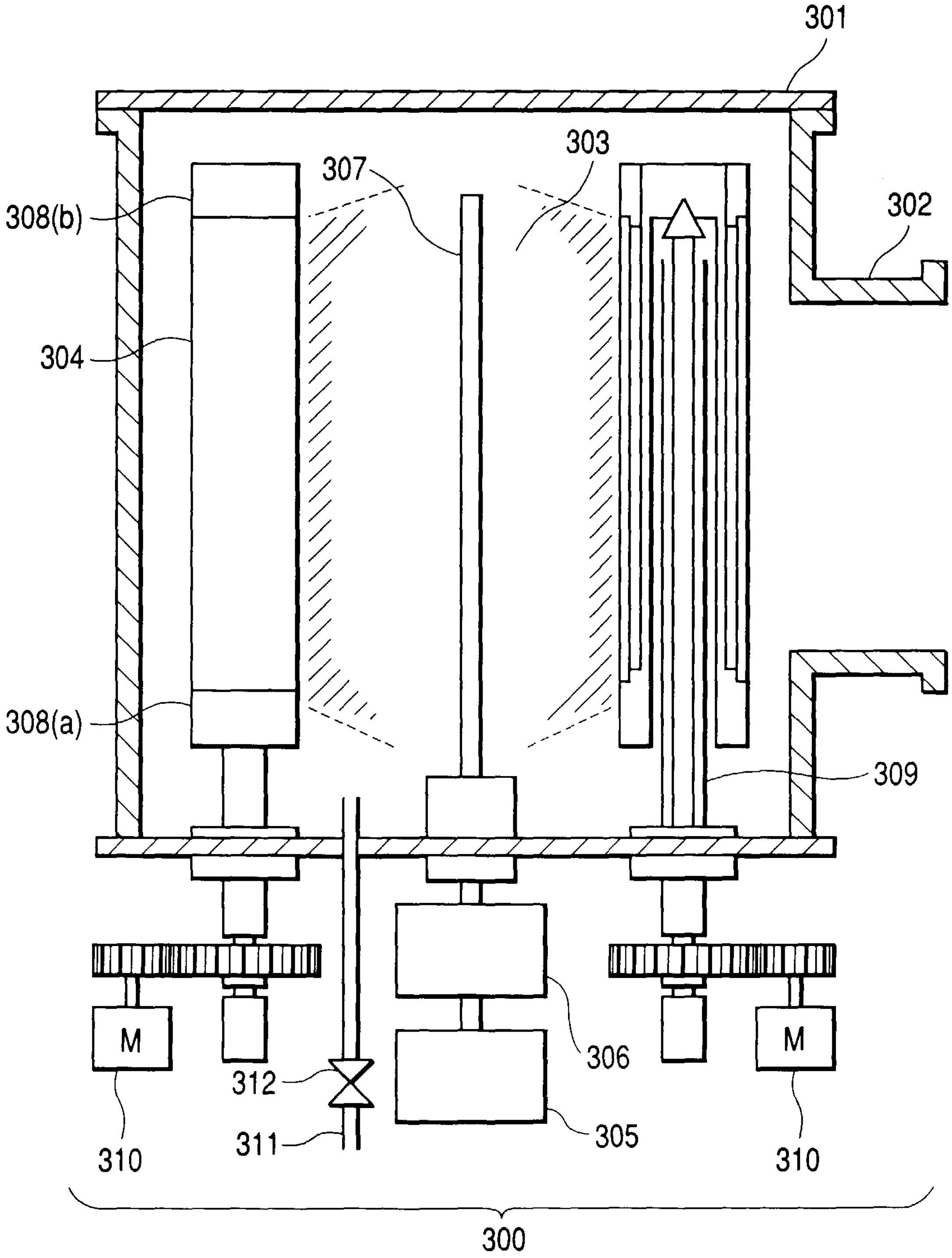
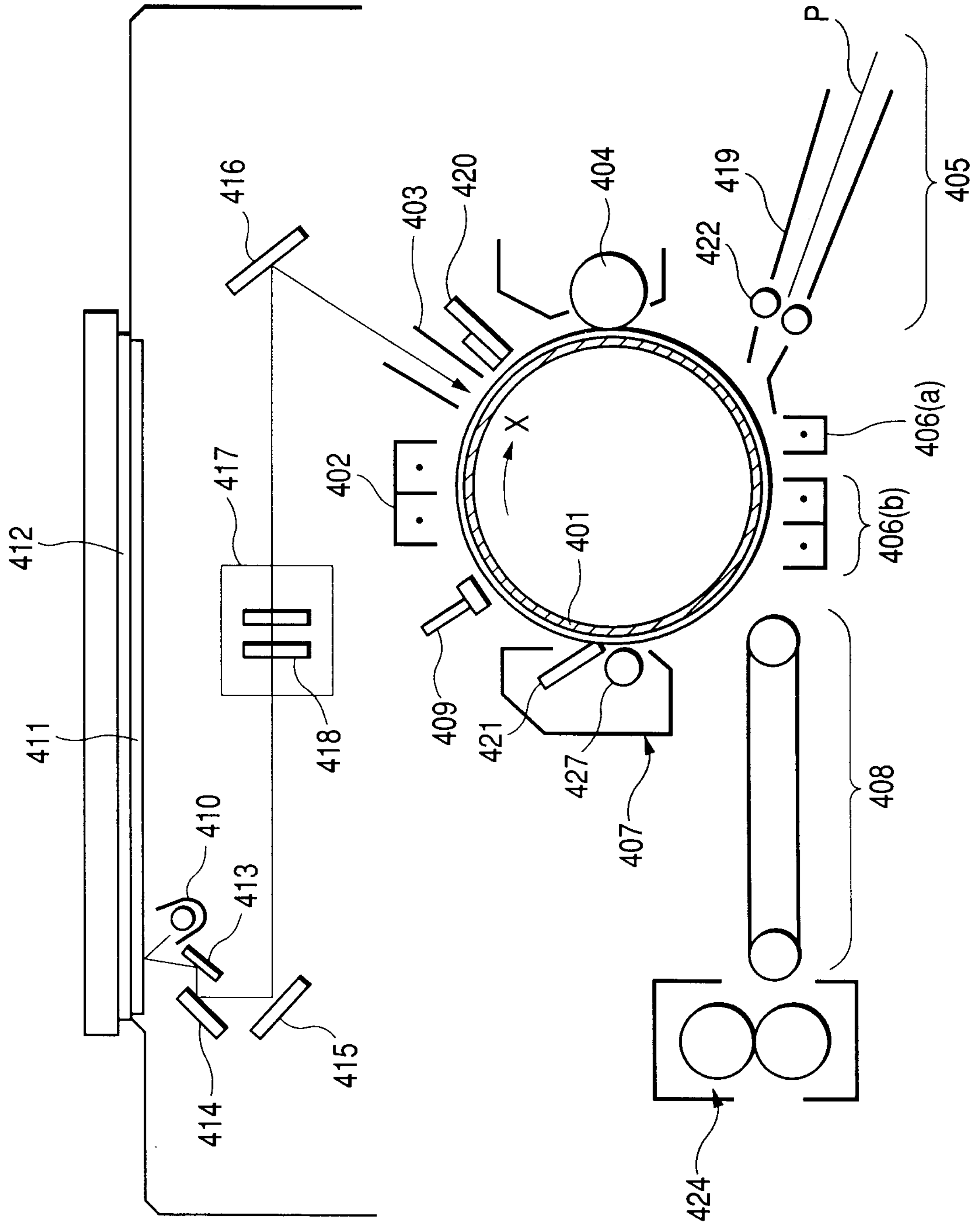


FIG. 4



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