HYDROPHOBIC CONDUCTIVE FILM AND PREPARATION AND USE THEREOF

TECHNICAL FIELD

The present application belongs to the technical field of semiconductor preparation, and specifically relates to a hydrophobic conductive film and preparation and use thereof.

BACKGROUND

A hydrophobic surface refers to a surface with a water contact angle greater than 90°. Hydrophobic surfaces have many excellent properties, such as waterproof and antifreeze, antibacterial and self-cleaning, anti-corrosion, and oil-water separation, and have potential application value in many fields.

Conventional methods for preparing hydrophobic surfaces include sol-gel method, microstructure processing, etc., but there are the following problems: 1) Sol-gel method usually uses dipping method and spin coating method for film formation. The uniformity of the films prepared by these two methods is poor, and the film needs to be dried or baked after film formation, which is apt to cause cracking or deformation of the film, and the film-base bonding force is poor and easy to fall off. 2) When preparing hydrophobic surfaces through microstructure processing, semiconductor processes such as lithography and etching are usually required, which have high requirements for equipment accuracy (line width, conformality, etc.). Based on the requirements of hydrophobicity, the microstructure surface cannot be encapsulated/protected, so it is very easy to be damaged in most application scenarios and cannot maintain high reliability. For some special optical devices, the surface micro-nano structure will affect the optical performance of the device. 3) The hydrophobic film is deposited using chemical vapor deposition (CVD) and atomic layer deposition (ALD) technology, but

the hydrophobicity is poor and cannot be used for most hydrophobic applications.

SUMMARY

In view of the above-mentioned problems existing in prior art, the first technical problem to be solved by the present invention is to provide a method for preparing a hydrophobic conductive film; the second technical problem to be solved by the present invention is to provide a hydrophobic conductive film prepared by the method; and the third technical problem to be solved by the present invention is to provide usages of the hydrophobic conductive film.

To solve the above problems, the present invention provides the following technical solutions:

In a first aspect, a method for preparing a hydrophobic conductive film comprises the following steps:

1) performing zinc-containing pre-surface treatment on a substrate surface in a vacuum and high-temperature reaction chamber to form the zinc atom saturated layer;

2) alternately introducing a zinc precursor and an oxygen precursor into the reaction chamber, and introducing an inert gas for purging, such that the zinc oxide film layer grows on the surface of the zinc atom saturated layer;

3) performing zinc-containing post-surface treatment on the zinc oxide film layer to form a zinc-containing transition layer; and

4) performing fluorination post-surface treatment on the zinc-containing transition layer to form a zinc fluoride surface layer.

In one embodiment of the present application, in step 1), the temperature of the reaction chamber is raised to 100-300°C., and a vacuum pump is used to maintain the reaction chamber in a vacuum state, and the substrate is placed in the reaction chamber.

In one embodiment of the present application, in step 1), the pressure of the

reaction chamber is maintained in a vacuum state of 0-5torr.

In one embodiment of the present application, in step 1), the substrate is first preheated in the reaction chamber to reach a required reaction temperature.

In one embodiment of the present application, in step 1), the zinc-containing pre-surface treatment comprises circulating the zinc precursor into the reaction chamber via an inert gas for multiple times.

In one embodiment of the present application, in step 1), when the substrate surface is subjected to zinc-containing pre-surface treatment, the temperature of the zinc precursor is 10-30°C, and an inert gas such as N_2 with a flow rate of 10-100sccm is introduced into the precursor as a carrier gas, the pulse time is 5-20s, the purge time is 10-20s, and the process is repeated for 30-50 cycles.

In one embodiment of the present application, in step 1), when the substrate surface is subjected to zinc-containing pre-surface treatment, the temperature of the zinc precursor is 10-30°C, and an inert gas such as N_2 with a flow rate of 10-100sccm is introduced into the precursor as a carrier gas, the pulse time is 10-20s, the purge time is 10-15s, and the process is repeated for 30-40 cycles.

In one embodiment of the present application, in step 1), when the substrate surface is subjected to zinc-containing pre-surface treatment, the temperature of the zinc precursor is 22°C, and an inert gas such as N_2 with a flow rate of 40sccm is introduced into the precursor as a carrier gas, the pulse time is 10s, the purge time is 15s, and the process is repeated for 40 cycles. The zinc precursor is selected from one of $Zn(DMP)_2$, $ZnCl_2$, $ZnMe_2$, $ZnEt_2$ or derivatives thereof.

In one embodiment of the present application, the zinc-containing pre-surface treatment of the substrate surface may increase the adsorption saturation of the first atomic layer to reach a state of supersaturation of zinc atoms.

In one embodiment of the present application, in step 2), the zinc oxide film is

prepared by a periodic atomic layer deposition process.

In one embodiment of the present application, in step 2), when the zinc oxide film is prepared by the periodic atomic layer deposition process, the process includes three preparation modes: DI-H_2O-ALD、O_2-Plasma-ALD or O_3-ALD.

In one embodiment of the present application, in step 2), the zinc precursor with an inert gas as a carrier gas and the oxygen precursor with an inert gas as a carrier gas are alternately introduced to the surface of the zinc atom saturated layer, and an inert gas is introduced for purging between the alternately introduced zinc precursor and oxygen precursor.

In one embodiment of the present application, in step 2), the zinc precursor with an inert gas as a carrier gas, prior to the oxygen precursor with an inert gas as a carrier gas, is introduced to the surface of the zinc atom saturated layer in sequence, and such alternate process is repeated until a zinc oxide film of a specified thickness is grown.

In one embodiment of the present application, in step 2), the oxygen precursor with an inert gas as a carrier gas, prior to the zinc precursor with an inert gas as a carrier gas, is introduced to the surface of the zinc atom saturated layer in sequence, and such alternate process is repeated until a zinc oxide film of a specified thickness is grown.

In one embodiment of the present application, in step 2), 10-200sccm of the inert gas is introduced for 1-20s to remove excess zinc precursor or oxygen precursor.

In one embodiment of the present application, in step 2), the inert gas may be one selected from the group consisting of nitrogen and argon.

In one embodiment of the present application, in step 2), the zinc precursor is one selected from the group consisting of $Zn(DMP)_2$, $ZnCl_2$, $ZnMe_2$, $ZnEt_2$ or derivatives thereof.

In one embodiment of the present application, in step 2), the inert gas and zinc precursor are introduced into the reaction chamber, and then the excess zinc precursor is purged with the inert gas and pumped out by a vacuum pump.

In one embodiment of the present application, in step 2), the inert gas such as N_2 is used as a carrier gas to introduce a zinc precursor such as $ZnEt_2$, $Zn(DMP)_2$, $ZnCl_2$ or $ZnMe_2$ into the reaction chamber with a set pulse duration of 0.1-2s, the temperature of the zinc precursor is 10-30℃, the inert gas is used to purge the zinc precursor for a duration of 5-25s and is pumped out of the reaction chamber by a vacuum pump.

In one embodiment of the present application, in step 2), the inert gas such as N_2 is used as a carrier gas to introduce a zinc precursor such as $ZnEt_2$, $Zn(DMP)_2$, $ZnCl_2$ or $ZnMe_2$ into the reaction chamber with a set pulse duration of 0.1-1s, the temperature of the zinc precursor is 10-30℃, the inert gas is used to purge the zinc precursor for a duration of 5-15s and is pumped out of the reaction chamber by a vacuum pump.

In one embodiment of the present application, in step 2), the inert gas such as N_2 is used as a carrier gas to introduce a zinc precursor such as $ZnEt_2$, $Zn(DMP)_2$, $ZnCl_2$ or $ZnMe_2$ into the reaction chamber with a set pulse duration of 0.3s, the temperature of the zinc precursor is 22℃, the inert gas is used to purge the zinc precursor for a duration of 10s and is pumped out of the reaction chamber by a vacuum pump.

The user can adaptively adjust the input parameters according to the specific introduced zinc precursor such as its derivatives.

In one embodiment of the present application, in step 2), the oxygen precursor is one selected from the group consisting of DI-H_2O, O_2-Plasma or O_3.

In one embodiment of the present application, in step 2), when the oxygen precursor is DI-H_2O, the temperature of DI-H_2O is maintained at 10-30°C, and the pulse time of DI-H_2O is 0.1-2s.

In one embodiment of the present application, in step 2), when the oxygen precursor is DI-H_2O, DI-H_2O is introduced into the reaction chamber, such that the substrate is exposed to the zinc precursor and DI-H_2O atmosphere in turn, ZnO is generated through a chemical reaction, and then an inert auxiliary gas is used to purge and remove undesirable side reactants, which are then pumped out through a vacuum pump, thereby forming a first layer of hydrophobic conductive film.

In one embodiment of the present application, after forming the first layer of hydrophobic conductive film, a zinc oxide monolayer of a fixed thickness is continuously deposited until a zinc oxide film layer is formed.

In one embodiment of the present application, in step 2), when the oxygen precursor is O_2-Plasma, the flow rate of O_2-Plasma is 100-200sccm, and the pulse time of O_2-Plasma is 5-15s.

In one embodiment of the present application, in step 2), when the oxygen precursor is O_2-Plasma, ionized O_2-Plasma is introduced into the reaction chamber, such that the substrate is exposed to the zinc precursor and O_2-Plasma atmosphere in turn, ZnO is generated through a chemical reaction, and then an inert auxiliary gas is used to purge and remove undesirable side reactants, which are then pumped out through a vacuum pump, thereby forming a first layer of hydrophobic conductive film.

In one embodiment of the present application, after forming the first layer of hydrophobic conductive film, a zinc oxide monolayer of a fixed thickness is continuously deposited until a zinc oxide film layer is formed.

In one embodiment of the present application, in step 2), when the oxygen precursor is O_3, the flow rate of O_3 is 100-300sccm, and the pulse time of O_3 is 2-10s.

In one embodiment of the present application, in step 2), when the oxygen precursor is O_3, O_3 is introduced into the reaction chamber, such that the substrate is

exposed to the zinc precursor and O_3 atmosphere in turn, ZnO is generated through a chemical reaction, and then an inert auxiliary gas is used to purge and remove undesirable side reactants, which are then pumped out through a vacuum pump, thereby forming a first layer of hydrophobic conductive film.

In one embodiment of the present application, after forming the first layer of hydrophobic conductive film, a zinc oxide monolayer of a fixed thickness is continuously deposited until a zinc oxide film layer is formed.

In one embodiment of the present application, the zinc oxide film layer is accumulated layer by layer on the surface of the substrate by using a zinc precursor and deionized water DI-H_2O/oxygen plasma O_2-Plasma/ozone O_3 under the coordinated action of source temperature, chamber temperature, chamber pressure and the flow rate of carrier gas in each pipeline.

In one embodiment of the present application, in step 3), during the zinc-containing post-surface treatment, the zinc precursor is introduced via a first carrier gas, the temperature of the zinc precursor is 10-30°C, the pulse time of the zinc precursor is 0.1-1s, the number of cycles is 10-30 cycles, and the flow rate of the first carrier gas is 10-100sccm.

In one embodiment of the present application, in step 3), during the zinc-containing post-surface treatment, the zinc precursor is introduced via a first carrier gas, the temperature of the zinc precursor is 24°C, the pulse time of the zinc precursor is 0.3s, the number of cycles is 20 cycles, and the flow rate of the first carrier gas is 30sccm.

In one embodiment of the present application, in step 3), the first carrier gas is an inert gas and can be selected from nitrogen or argon.

In one embodiment of the present application, in step 3), the zinc-containing post-surface treatment of the prepared zinc oxide film layer may effectively increase the surface roughness of the last atomic layer of ZnO, form a fluorinated transition layer,

and increase the adhesion of the fluorinated layer.

In one embodiment of the present application, in step 4), during the fluorination post-surface treatment, the fluorine precursor is introduced through the second carrier gas, the flow rate of the second carrier gas is 10-100sccm, the pulse time of the fluorine precursor is 0.1-2s, and the number of cycles is 20-40 cycles.

In one embodiment of the present application, in step 4), during the fluorination post-surface treatment, the fluorine precursor is introduced through the second carrier gas, the flow rate of the second carrier gas is 30-100sccm, the pulse time of the fluorine precursor is 0.5-2s, and the number of cycles is 30-40 cycles.

In one embodiment of the present application, in step 4), during the fluorination post-surface treatment, the fluorine precursor is introduced through the second carrier gas, the flow rate of the second carrier gas is 60sccm, the pulse time of the fluorine precursor is 1s, and the number of cycles is 40 cycles.

In one embodiment of the present application, in step 4), the fluorine precursor includes TIF_4 or derivatives thereof.

In one embodiment of the present application, in step 4), the second carrier gas is an inert gas and can be selected from nitrogen or argon.

In a second aspect of one embodiment of the present application, provided is a hydrophobic conductive film prepared by the above method, wherein the hydrophobic conductive film comprises, from bottom to top, a zinc atom saturated layer, a zinc oxide film layer, a zinc-containing transition layer and a zinc fluoride surface layer.

In one embodiment of the present application, the thickness of the hydrophobic conductive film is 5-50nm.

In one embodiment of the present application, the thickness of the hydrophobic conductive film is 10-40nm.

In one embodiment of the present application, the thickness of the hydrophobic

conductive film is 40nm.

In one embodiment of the present application, the hydrophobic conductive film is a hydrophobic conductive film with a thickness of 40 nm prepared by O_3 as an oxygen precursor.

In a third aspect, provided is a composite substrate comprising a substrate and a hydrophobic conductive film composited on the surface of the substrate.

In a fourth aspect, the use of the hydrophobic conductive film or the composite substrate in the preparation of electronic devices also falls into the protection scope of the present invention.

Compared with prior art, the present invention has the following beneficial effects:

(1) The present invention discloses a method for forming a ZnO hydrophobic conductive film on a substrate based on an atomic layer deposition (ALD) process. First, the substrate is subjected to zinc-containing pre-surface treatment to effectively increase the adsorption saturation of the first atomic layer, thereby increasing the heterogeneity of the ZnO film generated by the reaction and increasing the hydrophobicity of the ZnO film. Then, by rationally utilizing zinc precursor and deionized water (DI-H_2O)/oxygen plasma (O_2-Plasma)/ozone (O_3), a zinc oxide film of a desired precise thickness is accumulated layer by layer on the surface of the substrate under the coordinated effects of source temperature, chamber temperature, chamber pressure and the flow of carrier gas in each pipeline. The prepared zinc oxide film is further subjected to zinc-containing post-surface treatment to effectively increase the surface roughness of the last atomic layer of ZnO and form a fluorinated transition layer, which not only effectively improves the hydrophobicity of the ZnO film, but also helps to increase the fluorination degree of the ZnO film and increase the adhesion of the fluorinated layer after subsequent fluorination post-surface treatment. Finally, fluorination post-surface treatment is carried out. Different from the conventional chemical fluorination reaction,

the present application adopts the ALD method for fluorination surface treatment, and performs fluorine substitution reaction on the supersaturated Zn atoms on the surface, which effectively increases the hydrophobicity of the sample surface; at the same time, the formed film layer has a smaller bandgap width, making it easier for electrons in the valence band to jump to the conduction band, thereby having better conductivity.

(2) The hydrophobic conductive film prepared in the present application is produced based on ALD, the ZnO film prepared thereby has the characteristics of high hydrophobicity, good film-base bonding (hard to fall off), high film reliability (no warping, cracking or deformation), good film density, precise and controllable thickness, good film uniformity, high step coverage, and high optical transmittance (small extinction coefficient k). Compared with microstructures, it has stronger stability, is compatible with various semiconductor packaging processes, can effectively resist environmental interference, and can be applied to a variety of hydrophobic scenarios and will not affect the optical performance of the device. For precision devices that require anhydrous process, they can be processed by use of O_2-Plasma-ALD and/or O_3-ALD.

BRIEF DESCRIPTION OF THE DRAWINGS

To more clearly illustrate technical solutions in embodiments of the present invention or prior art, a brief introduction will be given below to the drawing needed to be used in the description of the embodiments or prior art. Obviously, the drawing in the following description are some embodiments of the present invention. For those of ordinary skilled in the art, other drawings can also be obtained based on these drawings without creative efforts.

FIG1 is a schematic diagram of the structure of a hydrophobic conductive film prepared in the present application;

FIG2 is a schematic diagram of the structure of a composite substrate prepared in

the present application;

FIG3 is a schematic diagram of a contact angle test of a hydrophobic conductive film prepared in Example 2;

FIG4 is a schematic diagram of a contact angle test of a hydrophobic conductive film prepared in Example 3;

FIG5 is a schematic diagram of a contact angle test of a hydrophobic conductive film prepared in Example 4;

FIG6 is a schematic diagram of a contact angle test of hydrophobic conductive films of different thicknesses prepared in Example 2;

FIG7 is a schematic diagram of a contact angle test of hydrophobic conductive films of different thicknesses prepared in Example 3; and

FIG8 is a schematic diagram of a contact angle test of hydrophobic conductive films of different thicknesses prepared in Example 4.

DETAIL DESCRIPTION OF THE INVENTION

The technical solutions in examples of the present application will be described clearly and completely below combined with the accompanying drawings of the embodiments of the present application. Obviously, the examples described are only some, but not all of the examples of the present application. Based on the examples of the present application, all other examples obtained by those skilled in the art without creative efforts shall fall within the protection scope of the present application.

The "range" disclosed in present application is defined in the form of a lower limit and an upper limit, and a given range is defined by selecting a lower limit and an upper limit, and the selected lower limit and upper limit define the boundaries of the particular range. Range defined in this way can be inclusive or exclusive of the end values, and can be arbitrarily combined, that is, any lower limit can be combined with any upper

limit to form a range.

Example 1

Provided is a method for forming a ZnO hydrophobic conductive film on a substrate based on an atomic layer deposition (ALD) process:

First, the reaction chamber was heated to 100-200°C; then the substrate was placed in the reaction chamber and preheated for 100-1000s to reach the reaction temperature; the substrate was subjected to zinc-containing pre-surface treatment, the temperature of the zinc precursor was maintained at 10-30°C, and an inert gas with a flow rate of 10-100sccm was introduced into the precursor as a carrier gas, the pulse time was 5-20s, the purge time was 10-20s, and the process was repeated for 30-50 cycles. Then, an inert gas was used as a carrier gas to introduce the zinc precursor into the reaction chamber with a set pulse duration of 0.1-2s, and an inert gas was used to purge the zinc precursor for a duration of 5-25s and was pumped out of the reaction chamber by a vacuum pump; deionized water (DI-H_2O) or O_2-Plasma (power 500-1500W) or O_3 precursor was further introduced into the reaction chamber to form Thermal ZnO, PE-ZnO or O_3-ZnO, and then an inert gas was used to purge and remove undesirable side reactants and was pumped out by a vacuum pump so as to form a first layer of zinc oxide film; finally, a zinc oxide film layer was obtained by periodic growth. Then, the prepared zinc oxide film was subjected to zinc-containing post-surface treatment, the temperature of the zinc precursor was maintained at 10-30°C, and an inert gas with a flow rate of 10-100sccm was introduced into the precursor as a carrier gas, the pulse time was 0.1-1s, and the process was repeated for 10-30 cycles. Finally, the ZnO film underwent the zinc-containing surface treatment was subjected to a fluorination post-surface treatment, and a fluorine precursor was introduced into the precursor via 10-100sccm of an inert gas as a carrier gas, the pulse time was 0.1-2s, and the process was repeated for 20-40 cycles to obtain a hydrophobic conductive film.

Among them, the inert gas may be selected from one of nitrogen and argon. The zinc precursor may be selected from one of $Zn(DMP)_2$, $ZnCl_2$, $ZnMe_2$, $ZnEt_2$ or derivatives thereof.

FIG1 is a schematic diagram of the structure of a hydrophobic conductive film 10 prepared in the present application, comprising, from bottom to top, a zinc atom saturated layer 11, a zinc oxide film layer 12, a zinc-containing transition layer 13 and a zinc fluoride surface layer 14.

FIG2 is a schematic diagram of the structure of a composite substrate prepared in the present application, comprising a substrate 20 and a hydrophobic conductive film 10 composited on the surface of the substrate 20, in which the hydrophobic conductive film 10 comprises a zinc atom saturated layer 11, a zinc oxide film layer 12, a zinc-containing transition layer 13 and a zinc fluoride surface layer 14.

Example 2

Provided is a method for forming a ZnO hydrophobic conductive film on a substrate based on an atomic layer deposition (ALD) process:

First, the reaction chamber was heated to 200°C; then the substrate was placed in the reaction chamber and preheated for 600s to reach the reaction temperature; the substrate was subjected to zinc-containing pre-surface treatment, the temperature of the zinc precursor was maintained at 22°C, and an inert gas N_2 with a flow rate of 40sccm was introduced into the precursor as a carrier gas, the pulse time was 10s, the purge time was 15s, and the process was repeated for 40 cycles. Then, N_2 was used as a carrier gas to introduce the zinc precursor $ZnEt_2$ into the reaction chamber with a set pulse duration of 0.3s, and N_2 was used to purge the zinc precursor for a duration of 10s and was pumped out of the reaction chamber by a vacuum pump; deionized water (DI-H_2O) precursor was further introduced into the reaction chamber to form Thermal ZnO, and then N_2 was used to purge and remove undesirable side reactants and was pumped out

by a vacuum pump so as to form a first layer of zinc oxide film; finally, a zinc oxide film layer was obtained by periodic growth. Then, the prepared zinc oxide film was subjected to zinc-containing post-surface treatment, the temperature of the zinc precursor was maintained at 24°C, and an inert gas with a flow rate of 30sccm was introduced into the precursor as a carrier gas, the pulse time was 0.3s, and the process was repeated for 20 cycles. Finally, the ZnO film underwent the zinc-containing surface treatment was subjected to a fluorination post-surface treatment, and a fluorine precursor TiF_4 was introduced into the precursor via 60sccm of an inert gas as a carrier gas, the pulse time was 1s, and the process was repeated for 40 cycles to obtain a hydrophobic conductive film.

Example 3

Provided is a method for forming a ZnO hydrophobic conductive film on a substrate based on an atomic layer deposition (ALD) process:

First, the reaction chamber was heated to 200°C; then the substrate was placed in the reaction chamber and preheated for 600s to reach the reaction temperature; the substrate was subjected to zinc-containing pre-surface treatment, the temperature of the zinc precursor was maintained at 22°C, and an inert gas N_2 with a flow rate of 40sccm was introduced into the precursor as a carrier gas, the pulse time was 10s, the purge time was 15s, and the process was repeated for 40 cycles. Then, N_2 was used as a carrier gas to introduce the zinc precursor $ZnEt_2$ into the reaction chamber with a set pulse duration of 0.3s, and N_2 was used to purge the zinc precursor for a duration of 10s and was pumped out of the reaction chamber by a vacuum pump; O_2-Plasma (power 500-1500W) was further introduced into the reaction chamber with a set pulse duration (8-12s), and it was purged by Ar for 10s and excess reaction gas was pumped out by a vacuum pump so as to form a first layer of PE-ZnO film; finally, a zinc oxide film layer was obtained by periodic growth. Then, the prepared zinc oxide film was subjected to zinc-containing

post-surface treatment, the temperature of the zinc precursor was maintained at 24°C, and an inert gas with a flow rate of 30sccm was introduced into the precursor as a carrier gas, the pulse time was 0.3s, and the process was repeated for 20 cycles. Finally, the ZnO film underwent the zinc-containing surface treatment was subjected to a fluorination post-surface treatment, and a fluorine precursor TiF_4 was introduced into the precursor via 60sccm of an inert gas as a carrier gas, the pulse time was 1s, and the process was repeated for 40 cycles to obtain a hydrophobic conductive film.

Example 4

Provided is a method for forming a ZnO hydrophobic conductive film on a substrate based on an atomic layer deposition (ALD) process:

First, the reaction chamber was heated to 200°C; then the substrate was placed in the reaction chamber and preheated for 600s to reach the reaction temperature; the substrate was subjected to zinc-containing pre-surface treatment, the temperature of the zinc precursor was maintained at 22°C, and an inert gas N_2 with a flow rate of 40sccm was introduced into the precursor as a carrier gas, the pulse time was 10s, the purge time was 15s, and the process was repeated for 40 cycles. Then, N_2 was used as a carrier gas to introduce the zinc precursor $ZnEt_2$ into the reaction chamber with a set pulse duration of 0.3s, and N_2 was used to purge the zinc precursor for a duration of 10s and was pumped out of the reaction chamber by a vacuum pump; O_3 (power 60%, O_3-flow rate 150-200sccm) was further introduced into the reaction chamber with a set pulse duration (2-8s), and it was purged by N_2 for 10s and excess reaction gas was pumped out by a vacuum pump so as to form a first layer of O_3-ZnO film; finally, a zinc oxide film layer was obtained by periodic growth. Then, the prepared zinc oxide film was subjected to zinc-containing post-surface treatment, the temperature of the zinc precursor was maintained at 24°C, and an inert gas with a flow rate of 30sccm was introduced into the precursor as a carrier gas, the pulse time was 0.3s, and the process was repeated for 20

cycles. Finally, the ZnO film underwent the zinc-containing surface treatment was subjected to a fluorination post-surface treatment, and a fluorine precursor TiF_4 was introduced into the precursor via 60sccm of an inert gas as a carrier gas, the pulse time was 1s, and the process was repeated for 40 cycles to obtain a hydrophobic conductive film.

Comparative example 1

First, the reaction chamber was heated to 200°C; then the substrate was placed in the reaction chamber and preheated for 600s to reach the reaction temperature, N_2 was used as a carrier gas to introduce the zinc precursor $ZnEt_2$ into the reaction chamber with a set pulse duration of 0.3s, and N_2 was used to purge the zinc precursor for a duration of 10s and was pumped out of the reaction chamber by a vacuum pump; deionized water (DI-H_2O) precursor was further introduced into the reaction chamber to form Thermal ZnO, and then N_2 was used to purge and remove undesirable side reactants and was pumped out by a vacuum pump so as to form a first layer of zinc oxide film; finally, a zinc oxide film layer was obtained by periodic growth.

Comparative example 2

First, the reaction chamber was heated to 200°C; then the substrate was placed in the reaction chamber and preheated for 600s to reach the reaction temperature; the substrate was subjected to zinc-containing pre-surface treatment, the temperature of the zinc precursor was maintained at 22°C, and an inert gas N_2 with a flow rate of 40sccm was introduced into the precursor as a carrier gas, the pulse time was 10s, the purge time was 15s, and the process was repeated for 40 cycles. Then, N_2 was used as a carrier gas to introduce the zinc precursor $ZnEt_2$ into the reaction chamber with a set pulse duration of 0.3s, and N_2 was used to purge the zinc precursor for a duration of 10s and was pumped out of the reaction chamber by a vacuum pump; deionized water (DI-H_2O) precursor was further introduced into the reaction chamber to form Thermal ZnO, and

then N_2 was used to purge and remove undesirable side reactants and was pumped out by a vacuum pump so as to form a first layer of zinc oxide film; finally, a zinc oxide film layer was obtained by periodic growth.

Comparative example 3

First, the reaction chamber was heated to 200°C; then the substrate was placed in the reaction chamber and preheated for 600s to reach the reaction temperature; the substrate was subjected to zinc-containing pre-surface treatment, the temperature of the zinc precursor was maintained at 22°C, and an inert gas N_2 with a flow rate of 40sccm was introduced into the precursor as a carrier gas, the pulse timewas 10s, the purge time was 15s, and the process was repeated for 40 cycles. Then, N_2 was used as a carrier gas to introduce the zinc precursor $ZnEt_2$ into the reaction chamber with a set pulse duration of 0.3s, and N_2 was used to purge the zinc precursor for a duration of 10s and was pumped out of the reaction chamber by a vacuum pump; deionized water (DI-H_2O) precursor was further introduced into the reaction chamber to form Thermal ZnO, and then N_2 was used to purge and remove undesirable side reactants and was pumped out by a vacuum pump so as to form a first layer of zinc oxide film; finally, a zinc oxide film layer was obtained by periodic growth. Then, the prepared zinc oxide film was subjected to zinc-containing post-surface treatment, the temperature of the zinc precursor was maintained at 24°C, and an inert gas with a flow rate of 30sccm was introduced into the precursor as a carrier gas, the pulse time was 0.3s, and the process was repeated for 20 cycles. A zinc oxide film underwent the zinc-containing post-surface treatment was obtained.

Comparative example 4

First, the reaction chamber was heated to 200°C; then the substrate was placed in the reaction chamber and preheated for 600s to reach the reaction temperature; N_2 was used as a carrier gas to introduce the zinc precursor $ZnEt_2$ into the reaction chamber

with a set pulse duration of 0.3s, and N_2 was used to purge the zinc precursor for a duration of 10s and was pumped out of the reaction chamber by a vacuum pump; O_2-Plasma (power 500-1500W) was further introduced into the reaction chamber with a set pulse duration (8-12s), and it was purged by Ar for 10s and excess reaction gas was pumped out by a vacuum pump so as to form a first layer of PE-ZnO film; finally, a zinc oxide film layer was obtained by periodic growth.

Comparative example 5

First, the reaction chamber was heated to 200°C; then the substrate was placed in the reaction chamber and preheated for 600s to reach the reaction temperature; the substrate was subjected to zinc-containing pre-surface treatment, the temperature of the zinc precursor was maintained at 22°C, and an inert gas N_2 with a flow rate of 40sccm was introduced into the precursor as a carrier gas, the pulse time was 10s, the purge time was 15s, and the process was repeated for 40 cycles. Then, N_2 was used as a carrier gas to introduce the zinc precursor $ZnEt_2$ into the reaction chamber with a set pulse duration of 0.3s, and N_2 was used to purge the zinc precursor for a duration of 10s and was pumped out of the reaction chamber by a vacuum pump; O_2-Plasma (power 500-1500W) was further introduced into the reaction chamber with a set pulse duration (8-12s), and it was purged by Ar for 10s and excess reaction gas was pumped out by a vacuum pump so as to form a first layer of PE-ZnO film; finally, a zinc oxide film layer was obtained by periodic growth.

Comparative example 6

First, the reaction chamber was heated to 200°C; then the substrate was placed in the reaction chamber and preheated for 600s to reach the reaction temperature; the substrate was subjected to zinc-containing pre-surface treatment, the temperature of the zinc precursor was maintained at 22°C, and an inert gas N_2 with a flow rate of 40sccm was introduced into the precursor as a carrier gas, the pulse time was 10s, the purge time

was 15s, and the process was repeated for 40 cycles. Then, N_2 was used as a carrier gas to introduce the zinc precursor $ZnEt_2$ into the reaction chamber with a set pulse duration of 0.3s, and N_2 was used to purge the zinc precursor for a duration of 10s and was pumped out of the reaction chamber by a vacuum pump; O_2-Plasma (power 500-1500W) was further introduced into the reaction chamber with a set pulse duration (8-12s), and it was purged by Ar for 10s and excess reaction gas was pumped out by a vacuum pump so as to form a first layer of PE-ZnO film; finally, a zinc oxide film layer was obtained by periodic growth. Then, the prepared zinc oxide film was subjected to zinc-containing post-surface treatment, the temperature of the zinc precursor was maintained at 24°C, and an inert gas with a flow rate of 30sccm was introduced into the precursor as a carrier gas, the pulse time was 0.3s, and the process was repeated for 20 cycles. A zinc oxide film underwent the zinc-containing post-surface treatment was obtained.

Comparative example 7

First, the reaction chamber was heated to 200°C; then the substrate was placed in the reaction chamber and preheated for 600s to reach the reaction temperature; N_2 was used as a carrier gas to introduce the zinc precursor $ZnEt_2$ into the reaction chamber with a set pulse duration of 0.3s, and N_2 was used to purge the zinc precursor for a duration of 10s and was pumped out of the reaction chamber by a vacuum pump; O_3 (power 60%, O_3-flow rate 150-200sccm) was further introduced into the reaction chamber with a set pulse duration (2-8s), and it was purged by N_2 for 10s and excess reaction gas was pumped out by a vacuum pump so as to form a first layer of O_3-ZnO film; finally, a zinc oxide film layer was obtained by periodic growth.

Comparative example 8

First, the reaction chamber was heated to 200°C; then the substrate was placed in the reaction chamber and preheated for 600s to reach the reaction temperature; the substrate was subjected to zinc-containing pre-surface treatment, the temperature of the

zinc precursor was maintained at 22°C, and an inert gas N_2 with a flow rate of 40sccm was introduced into the precursor as a carrier gas, the pulse time was 10s, the purge time was 15s, and the process was repeated for 40 cycles. Then, N_2 was used as a carrier gas to introduce the zinc precursor $ZnEt_2$ into the reaction chamber with a set pulse duration of 0.3s, and N_2 was used to purge the zinc precursor for a duration of 10s and was pumped out of the reaction chamber by a vacuum pump; O_3 (power 60%, O_3-flow rate 150-200sccm) was further introduced into the reaction chamber with a set pulse duration (2-8s), and it was purged by N_2 for 10s and excess reaction gas was pumped out by a vacuum pump so as to form a first layer of O_3-ZnO film; finally, a zinc oxide film layer was obtained by periodic growth.

Comparative example 9

First, the reaction chamber was heated to 200°C; then the substrate was placed in the reaction chamber and preheated for 600s to reach the reaction temperature; the substrate was subjected to zinc-containing pre-surface treatment, the temperature of the zinc precursor was maintained at 22°C, and an inert gas N_2 with a flow rate of 40sccm was introduced into the precursor as a carrier gas, the pulse time was 10s, the purge time was 15s, and the process was repeated for 40 cycles. Then, N_2 was used as a carrier gas to introduce the zinc precursor $ZnEt_2$ into the reaction chamber with a set pulse duration of 0.3s, and N_2 was used to purge the zinc precursor for a duration of 10s and was pumped out of the reaction chamber by a vacuum pump; O_3 (power 60%, O_3-flow rate 150-200sccm) was further introduced into the reaction chamber with a set pulse duration (2-8s), and it was purged by N_2 for 10s and excess reaction gas was pumped out by a vacuum pump so as to form a first layer of O_3-ZnO film; finally, a zinc oxide film layer was obtained by periodic growth. Then, the prepared zinc oxide film was subjected to zinc-containing post-surface treatment, the temperature of the zinc precursor was maintained at 24°C, and an inert gas with a flow rate of 30sccm was introduced into the

precursor as a carrier gas, the pulse time was 0.3s, and the process was repeated for 20 cycles. A zinc oxide film underwent the zinc-containing post-surface treatment was obtained.

The test results of the contact angles of the films prepared in Examples 2 to 4 and Comparative examples 1 to 9 (films with a thickness of 40 nm were selected for testing) are shown in Table 1 below.

The contact angle was tested using the sessile drop method by an optical contact angle measuring instrument. A droplet was placed on the film sample, and the image of the droplet was captured by a high-resolution camera, and then the angle was automatically measured by the software.

Table 1 Contact angles of 40 nm films prepared in different examples and comparative examples

	ALD Growth Mode	Zinc-containing pre-surface treatment	Zinc-containing post-surface treatment	Fluorination post-surface treatment	Contact angle
Example 2	DI-H_2O	√	√	√	119.59°
Comparative example 1	DI-H_2O	×	×	×	73.16°
Comparative example 2	DI-H_2O	√	×	×	76.31°
Comparative example 3	DI-H_2O	√	√	×	90.76°
Example 3	O_2-Plasma	√	√	√	120.16°

Comparative example 4	O_2-Plasma	×	×	×	75.16°
Comparative example 5	O_2-Plasma	√	×	×	84.36°
Comparative example 6	O_2-Plasma	√	√	×	94.00°
Example 4	O_3	√	√	√	122.74°
Comparative example 7	O_3	×	×	×	75.05°
Comparative example 8	O_3	√	×	×	90.76°
Comparative example 9	O_3	√	√	×	96.73°

FIGs 3-5 are schematic diagrams of the contact angle test of hydrophobic conductive films prepared in Examples 2-4. When the film thickness is 40 nm, the contact angles are 119.59°, 120.16°, and 122.74°, respectively.

FIGs 6-8 are schematic diagrams of the contact angle test of hydrophobic conductive films of different thicknesses prepared in Examples 2-4. It can be seen from the figures that as the film thickness grows from 10nm to 40nm, its hydrophobicity becomes better.

The test results of the sheet resistance Rs and resistivity P of the films (40nm) obtained in Example 4 and Comparative example 9 are shown in Table 2 below.

A digital four-probe tester is used to detect the sheet resistance and resistivity of the film. The digital four-probe tester consists of a host, a test bench, a four-probe

probe, a computer and other parts. The measurement data can be directly displayed by the host, or the computer can be controlled to collect the test data into the computer for analysis, and then the test results are statistically analyzed and displayed in a table form.

In a room temperature environment, the film sample is placed on the sample bench of the four-probe tester, and the probe is manually adjusted and pressed down to the sample surface. The sheet resistance value of the film is tested after calibration. The corresponding resistivity is calculated by the sheet resistance value.

Table 2 Effect of fluorination post-surface treatment on the sheet resistance Rs and resistivity P of the film

	With fluorination post-surface treatment		Without fluorination post-surface treatment	
Test site	Rs（Ω/□）	P（μΩ·cm）	Rs（Ω/□）	P（μΩ·cm）
1	205	79.4	291	203.7
2	210	79.5	465	381.3
3	210	53.2	266	263.3
4	210	72.6	274	213.7
5	212	52.6	399	375.1
6	212	72.4	348	285.4
7	207	42.5	288	265
8	204	57.7	276	215.3
9	214	60.6	372	282.7
Average	209.33	63.4	331	276.2

From the data in Table 2, it can be seen that the conductivity of the film is significantly increased after fluorination surface treatment.

From the data in Tables 1 and 2, it can be seen that the 40nm film prepared by O_3 growth mode after zinc-containing pre-surface treatment, zinc-containing post-surface treatment and fluorination post-surface treatment has excellent hydrophobicity and conductivity.

It should also be noted that in this document, relational terms such as first and second are merely used to distinguish one entity or operation from another and do not necessarily require or imply any such actual relationship or sequence between these entities or operations. Moreover, the terms "include", "comprises" or any other variants thereof are intended to cover non-exclusive inclusions.

The above application is described in detail in conjunction with specific embodiments and exemplary examples, but these descriptions cannot be understood as limitations on the present application. Those skilled in the art understand that without departing from the spirit and scope of the present application, the technical solution of the present application and its embodiments can be subjected to a variety of equivalent substitutions, modifications or improvements, all of which fall within the scope of the present application. The protection scope of the present application shall be subject to the attached claims.

CLAIMS:

1. A hydrophobic conductive film, wherein the hydrophobic conductive film (10) comprises, from bottom to top, a zinc atom saturated layer (11), a zinc oxide film layer (12), a zinc-containing transition layer (13) and a zinc fluoride surface layer (14).

2. A method for preparing the hydrophobic conductive film according to claim 1, comprising the following steps:

1) performing zinc-containing pre-surface treatment on a substrate surface to form the zinc atom saturated layer;

2) alternately introducing a zinc precursor and an oxygen precursor into a reaction chamber, and introducing an inert gas for purging, such that the zinc oxide film layer grows on the surface of the zinc atom saturated layer;

3) performing zinc-containing post-surface treatment on the zinc oxide film layer to form a zinc-containing transition layer; and

4) performing fluorination post-surface treatment on the zinc-containing transition layer to form a zinc fluoride surface layer.

3. The method according to claim 2, wherein in step 1), when the substrate surface is subjected to zinc-containing pre-surface treatment, the temperature of the zinc precursor is 10-30°C, the pulse time of the zinc precursor is 5-20s, and the number of cycles is 30-50 cycles.

4. The method according to claim 2, wherein in step 2), the zinc precursor with an inert gas as a carrier gas and the oxygen precursor with an inert gas as a carrier gas are alternately introduced into the reaction chamber, and an inert gas is introduced for purging between the alternately introduced zinc precursor and oxygen precursor, such that the zinc oxide film layer grows on the surface of the zinc atom saturated layer.

5. The method according to claim 2, 3 or 4, wherein the zinc precursor is one selected from the group consisting of $Zn(DMP)_2$, $ZnCl_2$, $ZnMe_2$, $ZnEt_2$ or derivatives thereof.

6. The method according to claim 2, wherein in step 2), the oxygen precursor is one selected from the group consisting of DI-H_2O, O_2-Plasma or O_3.

7. The method according to claim 6, wherein when the oxygen precursor is DI-H_2O, the temperature of DI-H_2O is maintained at 10-30°C, and the pulse time of DI-H_2O is 0.1-2s; when the oxygen precursor is O_2-Plasma, the flow rate of O_2-Plasma is 100-200sccm, and the pulse time of O_2-Plasma is 5-15s; when the oxygen precursor is O_3, the flow rate of O_3 is 100-300sccm, and the pulse time of O_3 is 2-10s.

8. The method according to claim 2, wherein in step 3), during the zinc-containing post-surface treatment, the zinc precursor is introduced via a first carrier gas, the temperature of the zinc precursor is 10-30°C, the pulse time of the zinc precursor is 0.1-1s, and the number of cycles is 10-30 cycles.

9. The method according to claim 2, wherein in step 4), during the fluorination post-surface treatment, a fluorine precursor is introduced via a second carrier gas, the pulse time of the fluorine precursor is 0.1-2s, and the number of cycles is 20-40 cycles.

10. The method according to claim 2, wherein the thickness of the hydrophobic conductive film is 5-50 nm.

11. The method according to claim 10, wherein the thickness of the hydrophobic conductive film is 10-40 nm.

12. A composite substrate comprising the hydrophobic conductive film according to claim 1, which comprises a substrate (20) and the hydrophobic conductive film (10) composited on the surface of the substrate (20).

13. Use of the hydrophobic conductive film according to claim 1 or the composite substrate according to claim 12 in the preparation of electronic devices.