Description

This invention relates to a method and apparatus for removing contaminants from a surface. More particularly, the invention relates to the removal of contaminants from a substrate surface through the application of energy from a high-energy source while the molecular structure of the surface being treated is preserved.

Surface contaminants include discrete pieces of matter that range in size from submicrons to granules visible to observation with the eye. Such contaminants may be fine dust or dirt particles or unwanted molecules comprised of elements such as carbon or oxygen. Contaminants frequently become adhered to a surface by weak covalent bonds, electrostatic forces, van der Waals forces, hydrogen bonding, coulombic forces or dipole-dipole interactions, making removal of the contaminants difficult.

In certain instances, the presence of surface contaminants renders the contaminated substrate less efficient or inoperable for the substrate's designated purpose. For example, in certain precise scientific measurement devices, accuracy is lost when optical lenses or mirrors in the devices become coated with microfine surface contaminants. Similarly in semiconductors, surface defects due to minor molecular contaminants often render semiconductor masks or chips worthless. Reducing the number of molecular surface defects in a quartz semiconductor mask by even a small amount can radically improve semiconductor chip production yields. Similarly, removing molecular surface contaminants, such as carbon or oxygen, from the surface of silicon wafers before circuit layers are deposited on the wafer or between deposition of layers significantly improves the quality of the computer chip produced.

The need for clean surfaces free of even the finest contaminants has led to the development of a variety of currently used surface cleaning methods. These known methods, however, each have their own serious drawbacks. For example, widely used chemical and mechanical cleaning techniques require the use of cleaning tools and agents that can introduce as many new contaminants to a treatment surface as they remove.

Another currently used method for cleaning substrate surfaces without outside agents requires that the treatment surface be melted to release contaminants which are then removed by ultra high vacuum pressure. This method has the disadvantage that the surface being treated must be briefly melted which may be undesirable, as for example when a semiconductor surface is cleaned between deposition of circuit layers and it is desired that the integrity of the previously deposited layers not be disturbed. A further disadvantage with this process is that ultra high vacuum equipment is both expensive and time consuming to operate.

Annealing treatment methods suffer similar drawbacks. When a surface is cleaned by annealing methods, the treatment surface of the substrate being cleaned is heated to a temperature that is generally below the melting point of the material being treated but high enough to enable rearrangement of the material's molecular crystal structure. The surface being treated is held at this elevated temperature for an extended period during which time the surface molecular structure is rearranged and contaminants are removed by ultra high vacuum. Annealing cleaning methods cannot be used where it is desired to preserve the integrity of the existing structure being cleaned.

Another currently utilized cleaning method, known as ablation, suffers from its own particular drawbacks. With ablation, a surface or contaminants on a surface are heated to the point of vaporization. Depending on the material being ablated, the material may melt before being vaporized or the material may sublimate directly on heating. With ablation cleaning techniques, if damage to the treatment surface is to be prevented, the ablation energy must be exactly aimed toward contaminants rather than the surface on which the contaminants lie, a difficult task when the contaminants are extremely small or randomly spaced. Even where the ablation energy can be successfully directed at a contaminant, it is difficult to vaporize the contaminant without also damaging the underlying treatment surface.

Surface cleaning by melting, annealing and ablation can be conducted with a laser energy source. However, using a laser energy source to remove contaminants from a surface by melting, annealing or ablation does not overcome the inherent disadvantages of these processes. For example, in U.S. Pat No. 4,292,093, "Method Using Laser Irradiation For the Production of Atomically Clean Crystalline Silicon and Germanium Surfaces" a surface region is irradiated in a non-reactive atmosphere with a plurality of laser pulses, each generating a melt front which moves through the region into the portion of the body contiguous with the region and back to the surface of said region. The laser annealing method disclosed requires both vacuum conditions and energy levels sufficient to cause rearrangement and melting of the treatment surface. Other known laser surface cleaning methods involving melting or annealing require similar high energy lasing and/or vacuum conditions, as disclosed in U.S. Pat. Nos. 4,181,538 and 4,680,616. Similarly the laser ablation technique disclosed in U.S. Pat. No. 3,464,534, "Laser Eraser" suffers the same

drawbacks as other high energy ablation methods.

Accordingly, it is an object of the invention to provide a method and apparatus for removing contaminants from a substrate surface that does not alter the molecular structure of the surface being treated, that does not melt or vaporize any portion of the surface being treated, that introduces no additional impurities to the substrate surface, and that does not require a vacuum and can be conducted economically in a very short period of time.

To achieve the objects and in accordance with the purpose of the invention, as embodied and as broadly described herein, a method and apparatus for removing surface contaminants from the surface of a substrate while preserving the molecular structure of the surface being treated is provided. The method includes the step of constantly flowing a gas across the substrate treatment surface and the step of irradiating the substrate with irradiation from a high-energy source, the irradiation having an energy density and duration between that required to release surface contaminants from the substrate treatment surface and that required to alter the molecular structure of the substrate treatment surface. Preferably, the irradiation from the high-energy source is pulsed laser irradiation. The method of the invention can be beneficially applied for removing surface contaminants from a semiconductor substrate before, between and after deposition of the circuitry layers on the semiconductor substrate.

The apparatus of the invention includes a gas inert to the substrate treatment surface, gas flow means for constantly flowing the gas across the treatment surface and a high-energy irradiation generating means for generating energy against the substrate treatment surface over which the gas passes. The high-energy irradiation generating means generates irradiation of an energy density and duration between that required to release surface contaminants from the substrate treatment surface and that required to alter the molecular structure of the substrate treatment surface. Preferably the high-energy irradiation generating means is a pulsed ultraviolet laser.

The accompanying drawings which are incorporated in and constitute a part of this specification, illustrate presently preferred embodiments of the invention and, together with the description, serve to explain the principles of the invention.

Fig. 1 is a schematic diagram of contaminant removal according to the invention:

Fig. 2 is a schematic diagram showing how laser irradiation is directed in one embodiment of the invention.

Fig. 3 is a schematic diagram showing how laser irradiation is directed in another embodiment of the invention.

Reference will now be made in detail to a presently preferred embodiment of the invention, an example of which is illustrated in the accompanying drawings. Throughout the drawings, like reference characters are used to designate like elements.

A method for removing surface contaminants from the surface of a substrate while preserving the molecular structure of the surface being treated is illustrated in Fig. 1. As shown in Fig. 1, an assembly 10 holds a substrate 12 from which surface contaminants are to be removed. A gas 18 from gas source 16 is constantly flowed over substrate 12. Gas 18 is inert to substrate 12 and is flowed across substrate 12 so as to bathe substrate 12 in a non-reactive gas environment. Preferably, gas 18 is a chemically inert gas such as helium, nitrogen or argon. An enclosure 15 for holding substrate 12 communicates with gas source 16 through a series of tubes 21, valves 22, and a gas flow meter 20.

Acccording to the embodiment of the invention shown in Fig. 1, enclosure 15 comprises a stainless steel sample reaction cell fitted with opposing gas inlet and outlet ports 23, 25 respectively. Enclosure 15 is fitted with a sealed optical grade quartz window 17 through which irradiation can pass. Inlet and outlet ports 23, 25 may comprise, for example, stainless steel tubing fitted with valves. After sample 12 is placed in enclosure 15, enclosure 15 is repeatedly flushed and backfilled with gas 18 and is kept at a pressure slightly above ambient atmospheric pressure to prevent inflow of other gases. Although enclosure 15 is shown as a solid chamber, it is anticipated that a surface being cleaned could be enclosed in any type of enclosure through which a gas can be flowed. For example, if the surface being treated is a large fixed object, a large portable enclosure such as a plastic bag might be utilized.

Flow of gas 18 may be regulated by flow meter 20 which, in the preferred embodiment, is a Matheson Model 602 flow meter. Valves 22 are preferably metering, regulating or bellows valves suitable for high temperature and pressure applications and for use with toxic, hazardous, corrosive or expensive gases or liquids, as for example Swagelok SS-4HTM series valves by Swagelok Co. of Solon, Ohio. Valves 22 can be opened or closed to isolate enclosure 15, to communicate enclosure 15 with gas source 16 or to put enclosure 15 in communication with another substance, such as a gas for depositing on substrate 12, coming from an alternate source 40.

According to the method of the invention, the substrate treatment surface is irradiated with high-energy irradiation characterized by an energy density and duration between that required to release surface contaminants from the substrate treatment surface and that required to alter the molecular structure of the substrate treatment surface. According to the preferred embodiment of the invention shown in Fig. 1, a laser 14 generates laser irradiation which is directed against the treatment surface of substrate 12. In Fig. 1, laser 14 is shown as being outside enclosure 15 and irradiating sample 12 through quartz window 17. However, it is contemplated that laser 14 could alternatively be placed within the enclosure 15.

The energy flux and the wavelength of the high-energy irradiation is preferably selected to be dependent upon the surface contaminants being removed. To this end, a gas analyzer 27 may be connected to outlet port 25. Analyzer 27 analyzes the contents of exhaust gas from enclosure 15 to facilitate selective energy and wavelength adjustment of laser 14. Gas analyzer 27 may be a mass spectrometer as for example a quadrapole mass spectrometer manufactured by Bruker Instruments, Inc. of Billerica, Massachusetts or by Perkin Elmer of Eden Prairie, Minnesota.

Selection of the high-energy irradiation source for use in the invention depends upon the desired irradiation energy and wavelength. The electron volt/photon (eV/photon) of the irradiation is preferably at least twice the energy necessary to break the bonds adhering the contaminants to the surface being cleaned. The bond energies between common contaminants such as carbon and oxygen, and common substrate materials such as silicon, titanium, germanium, iron, platinum and aluminum range between 2 and 7 eV/bond as disclosed in Handbook of Chemistry adn Physics, 68th ed., pp. F-169 to F-177 (CRC Press 1987). Accordingly, lasers emitting photons with energies in the range of 4 to 14 eV/photons are desirable. The wavelength should be below the wavelength that would compromise the integrity of the substrate surface by the photoelectric effect, as described in G.W. Castellan, Physical Chemistry, 2d ed., 458-459 (Academic Press, 1975). The preferred wavelength depends on the molecular species being removed and the resonance states of such species. The wavelengths and photon energies of a number of lasers operable in the invention are listed below.

TABLE I

Laser	Wavelength (nm)	eV/photon
XeCl, pulsed	308	4.04
argon-ion, continuous wave	257	4.83
KrF, pulsed	248	5.01
ArF, pulsed	193	6.44
Tunable dye lasers, pulsed or continuous wave	200-800	1.55-6.22

These lasers are described in greater detail in the following references: M.J. Webber ed., CRC Handbook of Laser Science, Vols. 1-5 (1982-1987); Mitsuo Maeda, Laser Dyes, (Academic Press 1984); and laser product literature from Lambda Physik at 289 Great Road, Acton, Massachusetts, Coherent, Inc. at 3210 Porter Drive, Palo Alto, California, and Spectra-Physics at 1250 West Middlefield Road, Mountain View, California. It is anticipated that high-energy xeon or mercury lamps or other types of lasers, including visible, ultraviolet, infared, x-ray or free electron lasers might be utilized as the irradiation source in the invention.

According to the invention, the irradiation directed against the substrate treatment surface has a power density less than that required to alter the molecular structure of the treatment surface from which contaminants are being removed. Preferably, the power density of the irradiation and the duration of the irradiation are selected so as to impart an amount of energy on the substrate surface that is significantly below the energy required for alteration of the substrate surface structure. The preferred energy level is dependent on the composition of the substrate being treated. For example, with certain substrate materials such as plastics, this energy level would be much lower than for other materials such as high strength carbide steels. The heats of formation for various materials are well known and are reported in the Handbook of Chemistry and Physics, 68th ed., pp. D33-D42 (CRC Press 1987). The heat of formation generally corresponds to the amount of heat required to break down various materials and can be used as a guideline in selecting a laser irradiation energy level and duration that will not alter the molecular structure of the surface being treated. The heats of formation of a number of common substrate materials are summarized in the following table.

TABLE II

Material	Heat of Formation	
Al_2O_3	16906.7 kgJ/mol;	17.52 eV/molecule
SiO_2	840.3 kgJ/mol;	9.11 eV/molecule
Nb_2O_5	1528.2 kgJ/mol;	13.27 eV/molecule
NiO	230.6 kgJ/mol;	2.50 eV/molecule
Ti_2O_3	500.2 kgJ/mol;	15.63 eV/molecule

The irradiation energy density and duration of irradiation used in the present invention is such that the heat of formation is not approached on the substrate treatment surface. Finding the maximum energy usable on a given substrate material will require some experimentation in light of the material's known heat of formation. Thus, annealing, ablation and melting are prevented from occurring.

When a substrate surface is irradiated as described above, the bonds and/or forces holding surface contaminants to the substrate surface are broken and the inert carrier gas carries contaminants away from the substrate surface during laser irradiation. As long as the cleaned substrate remains in the inert gas environment, new contaminants will not form on the substrate surface. If necessary, a suitable trapping system may be connected to enclosure outlet 25 for trapping and neutralizing removed contaminant species.

A substrate being treated may be selectively exposed to the laser irradiation by a variety of methods. As shown in Fig. 2, for example, substrate 12 is fixed on an XY table 13 which is selectively moved with respect to a fixed beam of laser pulses 11 that are directed through a beam splitter 24 and a focusing lens 28 before contacting selected portions of the surface of substrate 12 over which inert gas 18 flows. Alternatively, as shown in Fig. 3, laser pulses 11 may be split by beam splitters 30, 32 into two sets of pulses which are selectively moved by adjusting mirrors 34-37 over the surface of substrate 12 on a fixed table 17. A laser power meter 26 allows for close monitoring of the laser power being applied to the substrate.

EXAMPLE I

The native oxide of silicon is necessary for the promotion of thin film growth on semiconductor sufaces. Unfortunately, when semiconductor surfaces of silicon oxide are exposed to the environment, carbon contaminants adhere weakly to the semiconductor surface. The presence of these contaminants greatly reduces the conductivity or the insulating nature of the thin film to be deposited.Therefore, in semiconductor production, great precautions are taken to minimize environmental exposure through the use of elaborate vacuum, chemical and mechanical techniques. Vacuum techniques are expensive especially if high or near ultra high vacuum is used to keep surfaces clean between processing steps. Chemical (wet & dry) and mechanical techniques can damage the substrate treatment surface and, if the substrate being treated is a processed integrated circuit, damage to the underlying structure may occur.

In an attempt to overcome these problems, a pulsed KrF excimer laser whose fundamental wavelength is 248 nm (UV range) was directed at the surface of a silicon substrate in a sealed box through which argon gas was flowed. In order to decrease surface carbon contamination and decrease carbon percentage associated with chemisorbed organometallic (trimethyl aluminum), a precursor to aluminum thin film formation in semiconductor production, irradiation of 35 mJ/cm^2 for 6000 laser shots at a 10 Hz repetition rate was applied to a silicon oxide substrate surface with the KrF excimer laser. The laser treated surfaces were exposed during a continuous flow of argon gas at a flow rate of 16 l/hr under a 1.03 x 10^3 torr backing regulator pressure. After treatment, XPS analysis showed the substrate exhibited a significant decrease in surface carbon from a pretreatment average surface carbon covering 30-45% of the substrate surface to an after treatment average surface carbon covering 19% of the substrate surface. The substrate surface itself showed no damage or alteration.

A surface treated with laser irradiation as described above and then exposed to an organometallic gas flow showed, by XPS analysis, that 20.8% of the substrate surface was covered with carbon as compared to 40-45% of the substrate surface that was covered with carbon after organometallic gas exposure on a non-laser treated surface. When the laser was applied, as described above, both prior to exposure to organometallic gas and again after gas exposure, only 8.9% of the surface was covered with carbon. Areas adjacent to the laser-exposed areas also exhibited some effects of the laser-cleaning treatment. Areas adjacent to the treated area showed a reduced carbon level of 12.7 percent. This effect probably is due to

the gaussian nature of the applied laser pulse.

Transfer of the wafer from the sample cell to the XPS analyzer was via an argon filled glove box. The silicon wafer was transferred to the XPS through an inert UHV transfer rod. This kept environmental exposure to a minimum.

Another wafer of silicon oxide, while exposed to argon gas as described above, was exposed to pulsed KrF eximer laser irradiation of 9 mJ/cm^2 for 6000 shots at a 10 Hz repitition rate. XPS analysis showed a surface carbon coverage of 40−45% both before and after laser treatment. Thus, irradiation at 9 mJ/cm^2 did not remove adsorbed surface carbon.

Another wafer of silicon oxide, while exposed to argon gas as described above, was exposed to pulsed KrF eximer laser irradiation of 300 mJ/cm^2 for 6000 shots at a 10 Hz repetition rate. At the end of treatment, the substrate surface had suffered significant damage, including a hole through the substrate. Thus, irradiation at 300 mJ/cm^2 altered the molecular structure of the substrate surface.

These examples show laser irradiation at an appropriate energy flux and wavelength can decrease surface contamination without damaging underlying surface or adjacent structures.

It is expected, in view of the heat of formation of SiO , that subjecting a silicon oxide substrate surface to pulsed KrF eximer laser irradiation of less than 100 mJ/cm^2 for 6000 shots at a 10 Hz repetition rate would not alter the molecular structure of the substrate. Pulsed KrF eximer laser irradiation of less than 75 mJ/cm^2 for 6000 shots at a 10 Hz repetition rate is expected not alter a silicon oxide substrate surface in any way.

EXAMPLE II

High energy optical components are difficult to fabricate for such technologies as laser fusion, x−ray lithography and UV excimer laser optics. Laser fusion and x−ray lithography technologies are used exclusively in "clean" environments. Excimer laser optics have a short work life span because with current commercial film deposition technology, it is difficult to fabricate films capable of withstanding prolonged high−energy fluxes.

A perennial problem with high energy optics is optical breakdown. This phenomena can be described as "the catastrophic evolution of damage influcted in a transparent medium in a strong laser field." Y.R. Shen, Principles of Nonlinear Optics, 1st ed., 528−540 (Wiley Interscience 1984). This phenomena occurs in solids as well as gases. With a solid, such as a high energy optic, optical breakdown is exacerbated by the presence of a surface defect such as scratches and pores in the bulk material. In most cases, optical breakdown is due to surface contamination such as adsorbed dust particles. The presence of these contaminants lowers the breakdown threshold which in turn limits the maximum laser power that can be used from a given laser system. This fact is a very important limitation regarding the pumping of a laser medium (solid state or gaseous) by an external pump Energy source. This, in turn, limits the laser power that can be used to transmit energy through optical windows, lenses and other optical components.

Optical breakdown, for example on a solid, is promoted by the presence of surface adhered contaminants. The interaction of a laser pulse train with a sufficient energy cross section may deposit enough energy to generate an "avalanche" ionization on the solid surface. This can form a surface plasma which may disintegrate the solid. The presence of contaminants effectively decreases the laser's efficiency and decreases its use in potential applications.

To overcome the above described problems, the contaminant removal method, as described in this application, can be used to remove adhered contaminants such as adsorbed dust. For example, to treat an optical component, the component is exposed to a continuous flow of argon gas during which time a pulse KrF eximer laser is directed at the surface of the optical component. The laser is tuned to an appropriate energy flux and wavelength that is considerably less than the high energy pulse required to promote ionization and subsequent plasma in high energy optics. The optical component surface is irradiated at the selected flux and wavelength for a duration sufficent to remove adsorbed contaminants.

Claims

1. A method for removing surface contaminants from the surface of a substrate while preserving the molecular structure of the surface being treated, comprising the steps of:

   constantly flowing a gas across the substrate treatment surface, said gas being inert to the substrate treatment surface; and

   irradiating said substrate with high−energy irradiation, said irradiation having an energy density and duration between that required to release surface contaminants from the substrate treatment

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the gaussian nature of the applied laser pulse.

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These examples show laser irradiation at an appropriate energy flux and wavelength can decrease surface contamination without damaging underlying surface or adjacent structures.

It is expected, in view of the heat of formation of SiO , that subjecting a silicon oxide substrate surface to pulsed KrF eximer laser irradiation of less than 100 mJ/cm^2 for 6000 shots at a 10 Hz repetition rate would not alter the molecular structure of the substrate. Pulsed KrF eximer laser irradiation of less than 75 mJ/cm^2 for 6000 shots at a 10 Hz repetition rate is expected not alter a silicon oxide substrate surface in any way.

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To overcome the above described problems, the contaminant removal method, as described in this application, can be used to remove adhered contaminants such as adsorbed dust. For example, to treat an optical component, the component is exposed to a continuous flow of argon gas during which time a pulse KrF eximer laser is directed at the surface of the optical component. The laser is tuned to an appropriate energy flux and wavelength that is considerably less than the high energy pulse required to promote ionization and subsequent plasma in high energy optics. The optical component surface is irradiated at the selected flux and wavelength for a duration sufficent to remove adsorbed contaminants.

Claims

1. A method for removing surface contaminants from the surface of a substrate while preserving the molecular structure of the surface being treated, comprising the steps of:

constantly flowing a gas across the substrate treatment surface, said gas being inert to the substrate treatment surface; and

irradiating said substrate with high – energy irradiation, said irradiation having an energy density and duration between that required to release surface contaminants from the substrate treatment

surface and that required to alter the molecular structure of the substrate treatment surface.

2. A method as claimed in claim 1, wherein said step of irradiating said substrate with high-energy irradiation comprises irradiating said substrate with laser-generated irradiation.

3. A method as claimed in claim 1, wherein said high-energy irradiation is a laser-generated irradiation.

4. A method as claimed in claim 3, further comprising the steps of:

analyzing the gas having passed across the substrate treatment surface during laser treatment to determine the composition of removed contaminants; and

adjusting the energy density and duration of said laser pulse irradiation to raise the treatment surface energy level above that required to break bonds between the analyzed surface contaminants and the treatment surface.

5. A method as claimed in claim 4 wherein said step of adjusting the energy density and duration of said laser pulse irradiation includes adjusting the energy density and duration of said laser pulse irradiation to raise the treatment surface energy level to between two and five times that required to break bonds between the analyzed surface contaminants and the treatment surface.

6. A method for removing chemisorbed molecular contaminants from the surface of a semiconductor substrate while preserving the substrate treatment surface, comprising the steps of:

constantly flowing a gas across the substrate treatment surface, said gas being inert to the substrate treatment surface; and

irradiating said substrate with a series of laser-generated pulses, said laser pulse series having a duration of at least 6000 pulses wherein each pulse has an energy density in the range of 35 to 75 mJ/cm^2.

7. A method as claimed in claim 6 wherein said semiconductor substrate treatment surface consists essentially of silicon.

8. A method as claimed in claim 6 wherein said semiconductor substrate treatment surface consists essentially of silicon with semiconductor circuitry layered thereon.

9. A method as claimed in claim 8 wherein said laser-generated irradiation has a duration of about 6000 pulses and an energy density of about 35 mJ/cm^2.

10. A method in accordance with claim 1 for removing molecular contaminants from the surface of a semiconductor substrate during production of the semiconductor while preserving the substrate treatment surface, comprising the steps of :

flowing a gas across the semiconductor substrate treatment surface, said gas being inert to the substrate treatment surface;

while flowing said gas inert to said substrate treatment surface, irradiating said substrate before deposition of circuitry on the semiconductor substrate treatment surface with laser-generated irradiation, said irradiation having an energy density and duration between that required to release surface contaminants from the substrate treatment surface and that required to alter the molecular structure of the substrate treatment surface;

depositing a circuitry layer on said semiconductor substrate treatment surface;

flowing a gas across said deposited layer, said gas being inert to the substrate treatment surface and said deposited layer;

while flowing said gas inert to said substrate treatment surface and deposited layer, irradiating said substrate treatment surface after deposition of circuitry thereon with laser-generated irradiation, said irradiation having an energy density and duration between that required to release surface contaminants from the substrate treatment surface and that required to alter the molecular structure of the substrate treatment surface.

11. A method as claimed in claim 10 wherein said substrate treatment surface consists essentially of silicon.

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12. A method as claimed in claim 12 wherein said laser-generated irradiation has a duration of about 6000 pulses and an energy density of about 35 mJ/cm^2.

13. An apparatus for removing adsorbed surface contaminants from the surface of a substrate (12) while preserving the substrate treatment surface, comprising:
a gas (18) inert to the substrate treatment surface;
gas flow means for constantly flowing said gas across the substrate treatment surface;
laser pulse generating means (14) for generating, against the substrate treatment surface over which said gas (18) passes, laser pulses (11) having an energy density between the energy required to break bonds between adsorbed surface contaminants and the treatment surface, and the energy required to alter the molecular structure of the substrate treatment surface.

14. An apparatus as claimed in claim 13, wherein said laser pulse generating means (14) has an ultraviolet energy source.

15. An apparatus as claimed in claim 13, wherein said laser pulse generating means (14) is a KrF excimer laser.

16. An apparatus as claimed in claim 13, wherein said gas flow means comprises:
an enclosure (15) in which the substrate (12) being treated can be placed, said enclosure (15) having an inlet port (23) and an outlet port (25), and
means for introducing said gas to said enclosure (23) through said inlet port.

17. An apparatus as claimed in claim 13, wherein said gas inert to the surface of said substrate (12) is a chemically inert gas.

18. An apparatus as claimed in claim 17, wherein said chemically inert gas is argon.

19. An apparatus as claimed in claim 13, further comprising gas analyzer means (27) for analyzing the gas having passed across the substrate treatment surface during laser energy generation against said treatment surface, said gas analyzer (27) means being for determining the composition of contaminants removed from said surface.

20. An apparatus as claimed in claim 16, further comprising gas analyzer means (27) for analyzing the gas having passed across the substrate treatment surface during laser energy generation against said treatment surface, said gas analyzer means (27) being for determining the composition of contaminants removed from said surface, said gas analyzer means (27) being connected to said enclosure outlet port.

Patentansprüche

1. Verfahren zum Entfernen von Oberflächenverunreinigungen von der Oberfläche eines Substrats, wobei die molekulare Struktur der Substratoberfläche erhalten bleibt, dadurch gekennzeichnet, daß :
- dauernd ein Gas über die Substratoberfläche strömt, das bezüglich der Substratoberfläche inert ist; und
- dieses Substrat mit energiereicher Strahlung bestrahlt wird, wobei die Energiedichte der Strahlung und die Bestrahlungsdauer ausreichen, um Oberflächenverunreinigen von der Substratoberfläche abzulösen, aber nicht ausreichen, um die molekulare Struktur der Substratoberfläche zu verändern.

2. Verfahren gemäß Anspruch 1, dadurch gekennzeichnet, daß bei der Bestrahlung des Substrats mit energiereicher Strahlung das Substrat mit einer von einem Laser erzeugten Strahlung bestrahlt wird.

3. Verfahren gemäß Anspruch 1, dadurch gekennzeichnet, daß die energiereiche Strahlung eine von einem Laser erzeugte Strahlung ist.

4. Verfahren gemäß Anspruch 3, dadurch gekennzeichnet, daß :

- das Gas, das während der Laserbehandlung über die Substratoberfläche geströmt ist, analysiert wird, um die Zusammensetzung der entfernten Verunreinigungen zu bestimmen; und
- die Energiedichte der Laserimpulsstrahlung und die Bestrahlungsdauer so eingestellt werden, daß das Energieniveau der Substratoberfläche über das Energieniveau angehoben wird, das erforderlich ist, um die Bindungen zwischen den analysierten Oberflächenverunreinigungen und der Substratoberfläche auf zubrechen.

5. Verfahren gemäß Anspruch 4, dadurch gekennzeichnet, daß bei der Einstellung der Energiedichte der Laserimpulsstrahlung und der Bestrahlungsdauer das Energieniveau der Substratoberfläche auf ein Energieniveau angehoben wird, das zwei- bis fünfmal so hoch ist wie das Energieniveau, das erforderlich ist, um die Bindungen zwischen den analysierten Oberflächenverunreinigungen und der Substratoberfläche aufzubrechen.

6. Verfahren zum Entfernen von chemisorbierten molekularen Verunreinigungen von der Oberfläche eines Halbleitersubstrats, wobei die Substratoberfläche erhalten bleibt, dadurch gekennzeichnet, daß :
   - dauernd ein Gas über die Substratoberfläche strömt, das bezüglich der Substratoberfläche inert ist; und
   - das Substrat mit einer Reihe von mit einem Laser erzeugten Impulsen bestrahlt wird, die eine Dauer von mindestens 6000 Impulsen hat, wobei jeder Impuls eine Energiedichte im Bereich von 35 bis 75 mJ/cm^2 hat.

7. Verfahren gemäß Anspruch 6, dadurch gekennzeichnet, daß die Halbleiter-Substratoberfläche im wesentlichen aus Silizium besteht.

8. Verfahren gemäß Anspruch 6, dadurch gekennzeichnet, daß die Halbleiter-Substratoberfläche im wesentlichen aus Silizium mit einer darauf aufgebrachten Halbleiterschaltung besteht.

9. Verfahren gemäß Anspruch 8, dadurch gekennzeichnet, daß die von einem Laser erzeugte Strahlung eine Dauer von ungefähr 6000 Impulsen und eine Energiedichte von ungefähr 35 mJ/cm^2 hat.

10. Verfahren gemäß Anspruch 1 zum Entfernen von molekularen Verunreinigungen von der Oberfläche eines Halbleitersubstrats während der Herstellung des Halbleiters, wobei die Substratoberfläche erhalten bleibt, dadurch gekennzeichnet, daß :
    - ein Gas über die Halbleiter-Substratoberfläche strömt, wobei dieses Gas bezüglich der Substratoberfläche inert ist;
    - während das bezüglich der Substratoberfläche interte Gas strömt, das Substrat mit einer von einem Laser erzeugten Strahlung bestrahlt wird, bevor die Schaltung auf der Halbleiter-Substratoberfläche abgeschieden wird, wobei die Energiedichte dieser Strahlung und die Bestrahlungsdauer ausreichen, um die Oberflächenverunreinigungen von der Substratoberfläche abzulösen, aber nicht ausreichen, um die molekulare Struktur der Substratoberfläche zu verändern;
    - eine Schaltungsschicht auf der Halbleiter-Substratoberfläche abgeschieden wird;
    - ein Gas über die abgeschiedene Schicht strömt, das bezüglich der Substratoberfläche und der abgeschiedenen Schicht inert ist;
    - während das bezüglich der Substratoberfläche und der abgeschiedenen Schicht inerte Gas strömt, die Substratoberfläche, nachdem die Schaltung darauf abgeschieden wurde, mit einer von einem Laser erzeugten Strahlung bestrahlt wird, wobei die Energiedichte dieser Strahlung und die Bestrahlungsdauer ausreichen, um die Oberflächenverunreinigungen von der Substratoberfläche abzulösen, aber nicht ausreichen, um die molekulare Struktur der Substratoberfläche zu verändern.

11. Verfahren gemäß Anspruch 10, dadurch gekennzeichnet, daß die Substratoberfläche im wesentlichen aus Silizium besteht.

12. Verfahren gemäß Anspruch 10, dadurch gekennzeichnet, daß die von einem Laser erzeugte Strahlung eine Dauer von ungefähr 6000 Impulsen und eine Energiedichte von ungefähr 35 mJ/cm^2 hat.

13. Vorrichtung zum Entfernen von adsorbierten Oberflächenverunreinigungen von der Oberfläche eines Substrats (12), wobei die Substratoberfläche erhalten bleibt, aus :
    - einem Gas (18), das bezüglich der Substratoberfläche inert ist;
    - einem Gasströmungsmittel, um das Gas dauernd über die Substratoberfläche strömen zu lassen;
    - einem Laserimpuls-Erzeugungsmittel (14), um Laserimpulse (11) zu erzeugen, die auf die Substratoberfläche auftreffen, über die das Gas (18) strömt, und die eine Energiedichte haben, die ausreicht, um die Bindungen zwischen den adsorbierten Oberflächenverunreinigungen und der Substratoberfläche aufzubrechen, aber nicht ausreicht, um die molekulare Struktur der Substratoberfläche zu verändern.

14. Vorrichtung gemäß Anspruch 13, dadurch gekennzeichnet, daß das Laserimpuls-Erzeugungsmittel (14) eine Energiequelle für ultraviolette Energie aufweist.

15. Vorrichtung gemäß Anspruch 13, dadurch gekennzeichnet, daß das Laserimpuls-Erzeugungsmittel (14) ein KrF-Excimerlaser ist.

16. Vorrichtung gemäß Anspruch 13, dadurch gekennzeichnet, daß das Gasströmungsmittel besteht aus :
    - einem Gehäuse (15), in dem das zu behandelnde Substrat (12) angeordnet werden kann, wobei dieses Gehäuse eine Einlaßöffnung (23) und eine Auslaßöffnung (25) aufweist, und
    - einem Mittel zum Einleiten des Gases in das Gehäuse (15) über die Einlaßöffnung (23).

17. Vorrichtung gemäß Anspruch 13, dadurch gekennzeichnet, daß das bezüglich der Oberfläche des Substrats (12) inerte Gas ein chemisch inertes Gas ist.

18. Vorrichtung gemäß Anspruch 17, dadurch gekennzeichnet, daß das chemisch inerte Gas Argon ist.

19. Vorrichtung gemäß Anspruch 13, dadurch gekennzeichnet, daß sie außerdem ein Gasanalysiermittel (27) zum Analysieren des Gases aufweist, das während der Bestrahlung der Substratoberfläche mit der von einem Laser erzeugten Strahlung über die Substratoberfläche strömte, wobei dieses Gasanalysiermittel (27) vorgesehen ist, um die Zusammensetzung der von der Substratoberfläche entfernten Verunreinigungen zu bestimmen.

20. Vorrichtung gemäß Anspruch 16, dadurch gekennzeichnet, daß sie außerdem ein Gasanalysiermittel (27) zum Analysieren des Gases aufweist, das während der Bestrahlung der Substratoberfläche mit der von einem Laser erzeugten Strahlung über die Substratoberfläche strömte, wobei dieses Gasanalysiermittel (27) vorgesehen ist, um die Zusammensetzung der von der Substratoberfläche entfernten Verunreinigungen zu bestimmen, und das Gasanalysiermittel (27) an die Gehäuse-Auslaßöffnung (25) angeschlossen ist.

Revendications

1. Procédé pour éliminer les contaminants de surface de la surface d'un substrat tout en préservant la structure moléculaire de la surface traitée, ledit procédé comprenant les étapes suivantes :
    faire passer continuellement un gaz sur la surface du substrat traité, ledit gaz étant inerte vis-à-vis de la surface du substrat traité; et
    irradier ledit substrat par un rayonnement à haute énergie, ladite irradiation ayant une densité énergétique et une durée comprises entre celle requise pour éliminer les contaminants de surface de la surface du substrat traité et celle requise pour modifier la structure moléculaire de la surface du substrat traité.

2. Procédé selon la revendication 1, dans lequel ladite étape d'irradiation dudit substrat à rayonnement à haute énergie comprend l'irradiation dudit substrat par un rayonnement produit par laser.

3. Procédé selon la revendication 1, dans lequel ledit rayonnement à haute énergie est un rayonnement produit par laser.

4. Procédé selon la revendication 1, comprenant en outre les étapes suivantes :
    analyse du gaz qui est passé sur la surface du substrat traité pendant le traitement par laser, afin

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de déterminer la composition des contaminants éliminés;et

réglage de la densité énergétique et de la durée dudit rayonnement à impulsions laser afin d'augmenter le niveau énergétique du traitement de la surface au-dessus de celui requis pour rompre les liaisons entre les contaminants de la surface analysée et la surface traitée.

5. Procédé selon la revendication 4, dans lequel ladite étape de réglage de la densité énergétique et de la durée dudit rayonnement à impulsions laser comprend le réglage de la densité énergétique et de la durée dudit rayonnement à impulsions laser afin d'augmenter le niveau énergétique de la surface à traiter entre deux et cinq fois celui requis pour rompre les liaisons entre les contaminants de la surface analysée et la surface traitée.

6. Procédé pour éliminer les contaminants dont les molécules sont chémisorbées de la surface d'un substrat semi-conducteur tout en préservant la surface du substrat traité, ledit procédé comprenant les étapes suivantes :

faire passer continuellement un gaz sur la surface du substrat traité, ledit gaz étant inerte vis-à-vis de la surface du substrat traité; et

irradier ledit substrat avec une série d'impulsions produites par laser, ladite série d'impulsions laser ayant une durée d'au moins 6000 impulsions et chaque impulsion ayant une densité énergétique comprise dans la gamme de 35 à 75 mJ/cm^2.

7. Procédé selon la revendication 6, dans lequel ladite surface de substrat semi-conducteur traité est constituée essentiellement de silicium.

8. Procédé selon la revendication 6, dans lequel ladite surface du substrat semi-conducteur traité est constituée essentiellement de silicium, sur lequel des circuits semi-conducteurs ont été déposés.

9. Procédé selon la revendication 8, dans lequel ledit rayonnement produit par laser a une durée d'environ 6000 impulsions et une densité énergétique d'environ 35 mJ/cm^2.

10. Procédé selon la revendication 1, pour éliminer les contaminants moléculaires de la surface d'un substrat semi-conducteur pendant la fabrication du semi-conducteur tout en préservant la surface du substrat traité, ledit procédé comprenant les étapes suivantes :

faire passer un gaz sur la surface du substrat semiconducteur traité, ledit gaz étant inerte vis-à-vis de la surface du substrat traité;

pendant le passage dudit gaz inerte sur la surface du substrat traité, irradier ledit substrat avant le dépôt des circuits sur la surface de substrat semi-conducteur traité avec un rayonnement produit par laser, ledit rayonnement ayant une densité énergétique et une durée comprises entre celle requise pour éliminer les contaminants de surface de la surface de substrat traité et celle requise pour modifier la structure moléculaire de la surface de substrat traité.

déposer une couche de circuit sur ladite surface de substrat semi-conducteur traité;

faire passer un gaz sur ladite couche déposée, ledit gaz étant inerte vis-à-vis de la surface de substrat traité et vis-à-vis de ladite couche déposée;

pendant le passage dudit gaz inerte sur la surface de substrat traité et sur la couche déposée, irradier ladite surface de substrat traité après dépôt des circuits sur celle-ci par un rayonnement produit par laser, ledit rayonnement ayant une densité énergétique et une durée comprises entre celle requise pour éliminer les contaminants de surface de la surface de substrat traité et celle requise pour modifier la structure moléculaire de la surface de substrat traité.

11. Procédé selon la revendication 10, dans lequel ladite surface de substrat traité est constituée essentiellement de silicium.

12. Procédé selon la revendication 12, dans lequel ledit rayonnement produit par laser a une durée d'environ 6000 impulsions et une densité énergétique d'environ 35 mJ/cm^2.

13. Appareil pour éliminer les contaminants adsorbés en surface de la surface d'un substrat (12) tout en préservant la surface du substrat traité, ledit appareil comprenant :

un gaz (18) inerte vis-à-vis de la surface du substrat traité;

un moyen pour débiter du gaz afin de faire passer continuellement ledit gaz sur la surface du

substrat traité;

un moyen (14) de production d'impulsions laser pour envoyer sur la surface du substrat traité sur laquelle passe ledit gaz (18) des impulsions laser (11) ayant une capacité énergétique comprise entre l'énergie requise pour rompre les liaisons entre les contaminants adsorbés en surface et la surface traitée et l'énergie requise pour modifier la structure moléculaire de la surface du substrat traité.

14. Appareil selon la revendication 13, dans lequel ledit moyen (14) pour produire des impulsions laser a une source d'énergie ultraviolette.

15. Appareil selon la revendication 13, dans lequel ledit moyen (14) pour produire des impulsions laser est un excimer KrF.

16. Appareil selon la revendication 13, dans lequel ledit moyen pour débiter du gaz comprend :

une enceinte (15) dans laquelle peut être placé le substrat (12) traité, ladite enceinte (15) ayant un orifice d'entrée (23) et un orifice de sortie (25); et

un moyen pour introduire ledit gaz dans ladite enceinte (23) par ledit orifice d'entrée.

17. Appareil selon la revendication 13, dans lequel ledit gaz inerte vis-à-vis de la surface dudit substrat (12) est un gaz chimiquement inerte.

18. Appareil selon la revendication 17, dans lequel ledit gaz chimiquement inerte est de l'argon.

19. Appareil selon la revendication 13, comprenant en outre un analyseur de gaz (27) pour analyser le gaz qui est passé sur la surface de substrat traité pendant la production d'énergie laser sur ladite surface traitée, ledit analyseur de gaz (27) servant à déterminer la composition des contaminants éliminés de ladite surface.

20. Appareil selon la revendication 16, comprenant en outre un analyseur de gaz (27) pour analyser le gaz qui est passé sur la surface du substrat traité pendant la production d'énergie laser sur ladite surface traitée, ledit analyseur de gaz (27) servant à déterminer la composition des contaminants éliminés de ladite surface, ledit analyseur de gaz (27) étant connecté audit orifice de sortie de l'enceinte.