

CONVENTION APPLICATION BY A ~~COMPANY~~ PERSON

FORM 8 - REGULATION 12 (2)

AUSTRALIA
PATENTS ACT 1952

DECLARATION IN SUPPORT OF A CONVENTION APPLICATION FOR A PATENT

In support of the Convention Application made by

(a) Here insert (in full)
Name of Company.

(a) AUDREY C. ENGELSBERG

(hereinafter referred to as "Applicant") for a patent for an invention entitled:

(b) Here insert Title of
Invention.

(b) REMOVAL OF SURFACE CONTAMINANTS BY IRRADIATION FROM A
HIGH-ENERGY SOURCE

(c) and (d) Here insert
Full Name and Address
of Company Official
authorised to make
declaration.

I, (c) AUDREY C. ENGELSBERG
of (d) 61-B Sherwood Forest, Wappingers Falls, New York 12590,
United States of America

do solemnly and sincerely declare as follows:

1. I am ~~authorised by Applicant to make this declaration on its behalf~~
the Applicant for the Patent.

2. The basic Application(s) as defined by section 141 of the Act was / were made

(e) Here insert Basic
Country followed by date
of Basic Application.

in (e) U.S.A. on the 8th day of July 1988

(f) Here insert Full
Name(s) of Applicant(s)
in Basic Country.

by (f) Audrey C. Engelsberg

in on the day of 19

by
in on the day of 19

by
in on the day of 19
by

3. ~~(f)~~ I am the actual Inventor.

(g) Here insert (in full)
Name and Address of
actual Inventor or
Inventors.

..... is/are
the actual inventor(s) of the invention and the facts upon which Applicant is entitled to make the
Application are as follows:

4. The basic Application(s) referred to in paragraph 2 of this Declaration was/were the first
Application(s) made in a Convention country in respect of the invention, the subject of the
Application.

DECLARED at MILTON, VT, USA

this 19th day of MARCH 1991

(h) Personal Signature
of Declarant (c) (no seal,
witness or legalisation).

(h) Audrey C. Engelsberg

(12) PATENT ABRIDGMENT (11) Document No. AU-B-38676/89
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 620766

(Modified Examination)

- (54) Title
REMOVAL OF SURFACE CONTAMINANTS BY IRRADIATION FROM A HIGH-ENERGY SOURCE
- International Patent Classification(s)
(51)⁴ **H01L 021/263 H01L 021/268**
(51)⁵ **B23K 026/00**
- (21) Application No. : **38676/89** (22) Application Date : **07.07.89**
- (87) PCT Publication Number : **WO90/00812**
- (30) Priority Data
- (31) Number (32) Date (33) Country
216903 08.07.88 US UNITED STATES OF AMERICA
- (43) Publication Date : **05.02.90**
- (44) Publication Date of Accepted Application : **20.02.92**
- (71) Applicant(s)
AUDREY C. ENGELSBERG
- (72) Inventor(s)
AUDREY C. ENGELSBERG
- (74) Attorney or Agent
SHELSTON WATERS , 55 Clarence Street, SYDNEY NSW 2000
- (56) Prior Art Documents
AU 38690/89 B23K 26/00 26/12
- (57) Claim

1. A method for removing surface contaminants from the surface of a substrate while preserving the crystal 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 characterized by an energy density and duration sufficient to release surface contaminants from the substrate treatment surface insufficient to alter the crystal structure of the substrate treatment surface.

PCT

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁴ :**H01L 21/263, 21/268****A1****(11) International Publication Number:****WO 90/00812****(43) International Publication Date:**

25 January 1990 (25.01.90)

(21) International Application Number: PCT/US89/02952**(22) International Filing Date:** 7 July 1989 (07.07.89)**(30) Priority data:**

216,903

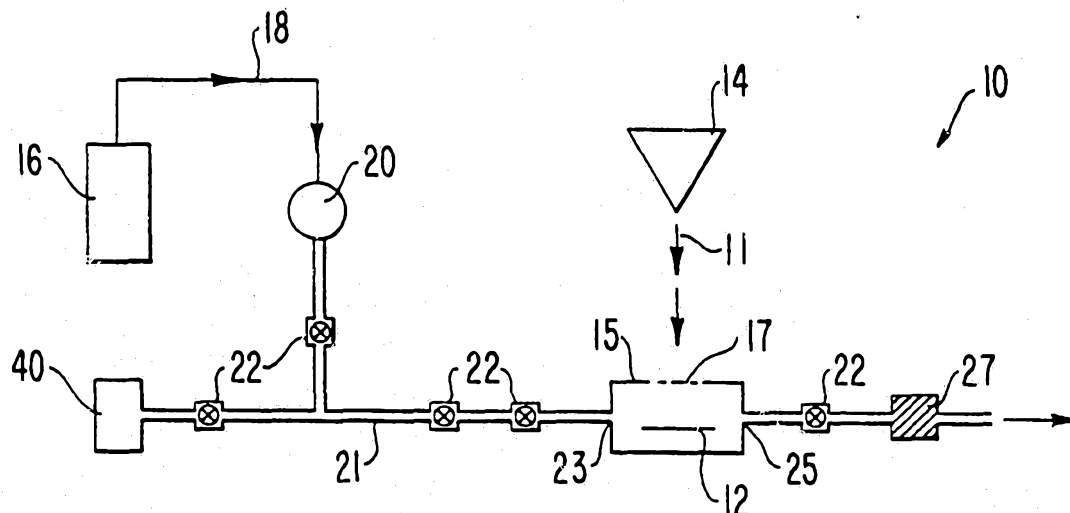
8 July 1988 (08.07.88)

US

(71)(72) Applicant and Inventor: ENGELSBURG, Audrey, C.
[US/US]; 61-B Sherwood Forest, Wappingers Falls, NY
12590 (US).**(74) Agent:** GORMAN, Thomas, W.; Howrey & Simon, 1730
Pennsylvania Avenue, N.W., Washington, DC 20006
(US).**(81) Designated States:** AU, BR, DK, FI, NO, SU.

Published

with international search report.

620766**(54) Title:** REMOVAL OF SURFACE CONTAMINANTS BY IRRADIATION FROM A HIGH-ENERGY SOURCE**(57) Abstract**

A method and apparatus for removing surface contaminants from the surface of a substrate (12) by high-energy irradiation is provided. The invention enables removal of surface contaminants without altering the substrate's underlying molecular structure. The source of high-energy irradiation may comprise a pulsed laser (14).

REMOVAL OF SURFACE CONTAMINANTS BY
IRRADIATION FROM A HIGH-ENERGY SOURCE
BACKGROUND OF THE INVENTION

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 crystal 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 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.

5 Depending on the material being ablated, the material may melt before being vaporized or the material may sublime directly on heating. With ablation cleaning techniques, if damage to the treatment surface is to be prevented, the ablation energy must be exactly aimed
10 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
15 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
20 ablation does not overcome the inherent disadvantage 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" the laser annealing method disclosed
25 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
30 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
35 to provide a method and apparatus for removing contaminants from a substrate surface that does not

alter the crystal structure of the surface being treated.

It is another object of the invention to provide a method and apparatus for removing contaminants from a treatment surface that does not melt or vaporize any portion of the surface being treated.

It is another object of the invention to provide a method and apparatus for removing contaminants from the surface of a substrate that introduces no additional impurities to the substrate surface.

It is a further object of the invention to provide a method and apparatus for cleaning a substrate surface that does not require a vacuum and can be conducted economically in a very short period of time.

Additional objects and advantages of the present invention will be set forth in part in the description that follows and in part will be obvious from the description or may be learned by practice of the invention. The objects and advantages of the invention may be realized and obtained by the method and apparatus particularly pointed out in the appended claims.

SUMMARY OF THE INVENTION

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 crystal 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 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 crystal 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

5 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

10 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

15 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 crystal structure of the substrate treatment surface.

20 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

25 embodiments of the invention and, together with the description, serve to explain the principles of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic diagram of contaminant

30 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.

DESCRIPTION OF THE PREFERRED EMBODIMENT

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 crystal 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.

According 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 crystal 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 quadrupole 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 and Physics, 68th ed., pp. F-169 to F-177 (CRC Press 1987) which is hereby incorporated by reference. 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) which is hereby incorporated by reference. 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

<u>Laser</u>	<u>Wavelength (nm)</u>	<u>eV/photon</u>
XeCl, pulsed	308	4.04
argon-ion,	257	4.83

35



	continuous wave		
	KrF, pulsed	248	5.01
	ArF, pulsed	193	6.44
5	Tunable dye lasers, pulsed or continuous wave	200-800	1.55-6.22

These lasers are described in greater detail in the following references which are hereby incorporated by reference: 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 xenon or mercury lamps or other types of lasers, including visible, ultraviolet, infrared, 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 crystal 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), which is hereby incorporated by reference. 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

<u>Material</u>	<u>Heat of Formation</u>
Al ₂ O ₃	16906.7 kgJ/mol; 17.52 eV/molecule
SiO ₂	840.3 kgJ/mol; 9.11 eV/molecule
Nb ₂ O ₅	1528.2 kgJ/mol; 13.27 eV/molecule
NiO	230.6 kgJ/mol; 2.50 eV/molecule
Ti ₂ O 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.

15 Example I

The native oxide of silicon is necessary for the promotion of thin film growth on semiconductor surfaces. 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
35 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/cm² 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 1.03×10^3 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 areas 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.

5 Another wafer of silicon oxide, while exposed to argon gas as described above, was exposed to pulsed KrF excimer laser irradiation of 9 mJ/cm^2 for 6000 shots at a 10 Hz repetition 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
10 remove adsorbed surface carbon.

Another wafer of silicon oxide, while exposed to argon gas as described above, was exposed to pulsed KrF excimer laser irradiation of 300 mJ/cm^2 for 6000 shots at a 10 Hz repetition rate. At the end of
15 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.

20 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_2 , that subjecting a silicon oxide
25 substrate surface to pulsed KrF excimer 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 excimer laser irradiation of less than 75 mJ/cm^2 for 6000 shots at a
30 10 Hz repetition rate is not expected to 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
35 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 inflicted 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 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 excimer 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 sufficient to remove adsorbed contaminants.

It will be apparent to those skilled in the art that modifications and variations can be made in the method and apparatus of removing surface contaminants of this invention. The invention in its broader aspects is, therefore, not limited to the specific details, representative methods and apparatus, and illustrative examples shown and described above. Thus, it is intended that all matter contained in the foregoing description or shown in the accompanying drawings shall be interpreted as illustrative and not in a limiting sense.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:-

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

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

10 irradiating said substrate with high-energy irradiation, said irradiation characterized by an energy density and duration sufficient to release surface contaminants from the substrate treatment surface insufficient to alter the crystal structure of the substrate treatment surface.

2. The method of claim 1 wherein said step of irradiating said substrate with high-energy irradiation comprises irradiating said substrate with laser-generated irradiation.

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

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

10 irradiating said substrate treatment surface with laser generated irradiation, said irradiation characterized by an energy density and duration sufficient to break bonds between adsorbed surface contaminants and the treatment surface, and insufficient to alter the crystal structure of the substrate treatment surface.



4. The method of claim 3, further comprising the steps of:

analyzing the gas having passed across the substrate treatment surface during laser treatment to
 5 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
 10 treatment surface.

5. The method of 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
 5 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:

5 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
 10 duration of at least 6000 pulses wherein each pulse has an energy density in the range of 35 to 75 mJ/cm².

7. The method of claim 6 wherein said semiconductor substrate treatment surface consists essentially of silicon.



8. The method of claim 6 wherein said semiconductor substrate treatment surface consists essentially of silicon with semiconductor circuitry layered thereon.

9. The method of claim 8 wherein said laser-generated irradiation has a duration of about 6000 pulses and an energy density of about 35 mJ/cm².

10. A method 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 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 crystal 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 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 crystal structure of the substrate treatment surface.

11. The method of claim 10 wherein said substrate treatment surface consists essentially of silicon.

12. The method of claim 10 wherein said laser-generated irradiation has a duration of about 6000 pulses and an energy density of about 35 mJ/cm^2 .

DATED this 15th day of AUGUST, 1991.

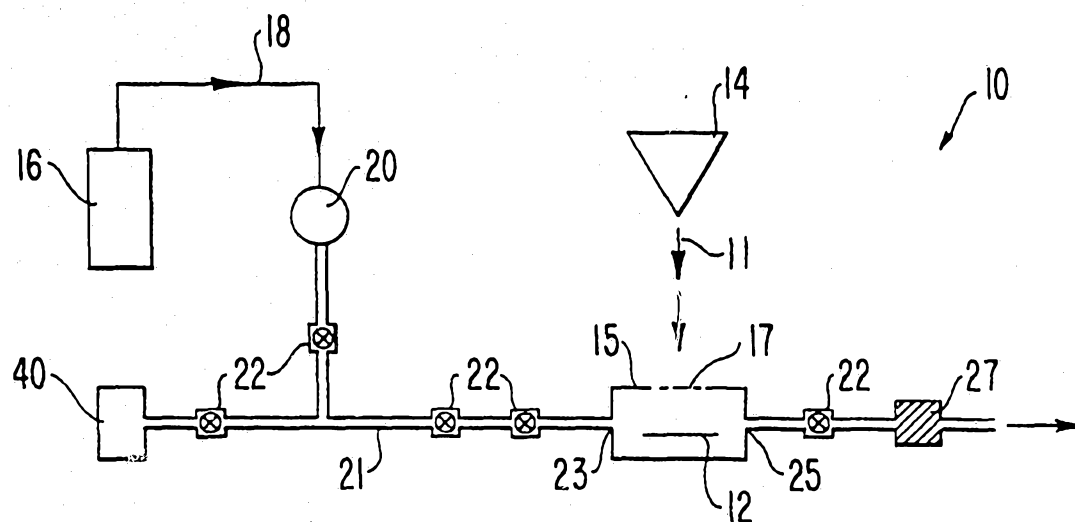
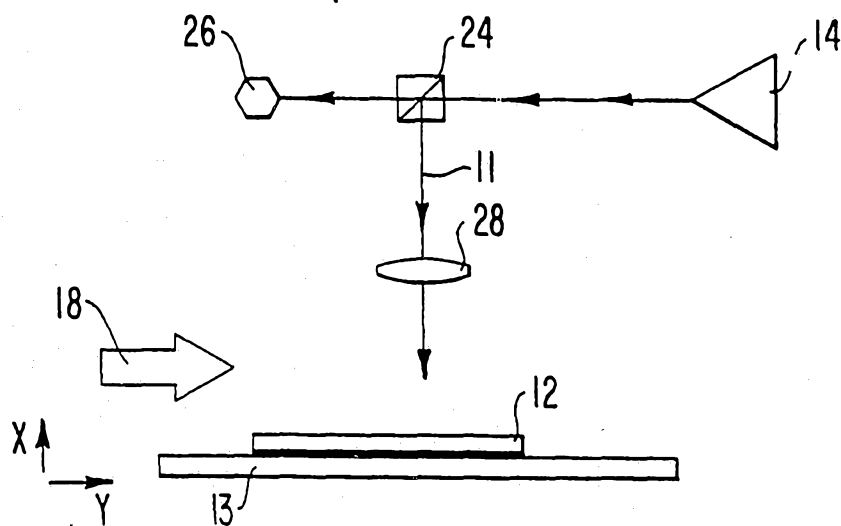
AUDREY C. ENGELSBERG

Attorney: PETER HEATHCOTE

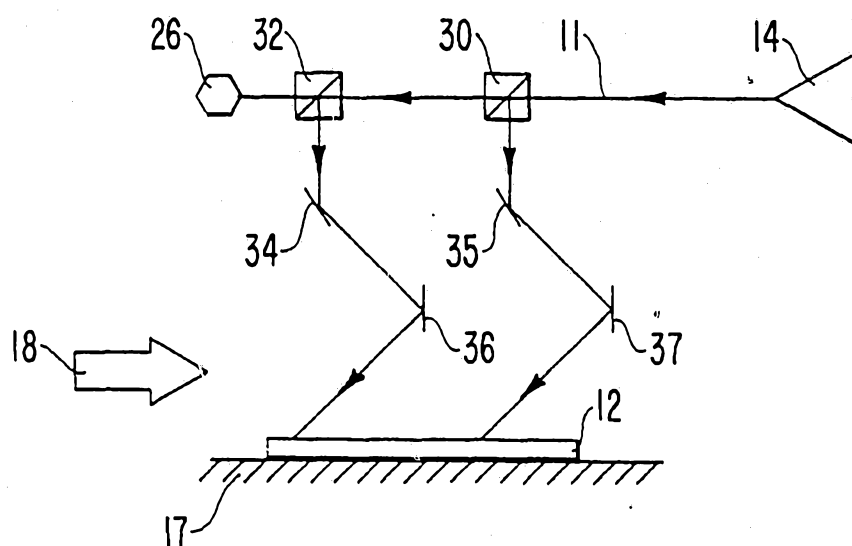
Fellow Institute of Patent Attorneys of Australia
of SHELSTON WATERS



1/2

FIG. 1**FIG. 2**

2/2

FIG. 3

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US89/02952

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC4: HOI 21/263, 21/268		
USCL: 437/19, 173, 247, 907, 908, 939, 942, 946, 148/DIG 17, 91, 92, 93, 94		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
US	437/19, 173, 247, 907, 908, 939, 942, 946; 148/DIG 17, DIG 91, DIG 92, DIG 93, DIG 94; 134/1,31	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹		
Category [*]	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	US,A, 3,364,087 (Solomon et al) 16 January 1968	1-20
A	US,A, 3,464,534 (Muncheryan) 02 September 1969	
A	US,A, 4,181,538 (Narayan et al) 01 January 1980	
A	US,A, 4,292,093 (Ownby et al) 29 September 1981	
A	US,A, 4,305,973 (Yaron et al) 15 December 1981	
Y	US,A, 4,668,304 (Schachamever et al) 26 May 1987. (See entire document).	
[*] Special categories of cited documents: ¹⁰ "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search		Date of Mailing of this International Search Report
05 September 1989		10 OCT 1989
International Searching Authority		Signature of Authorized Officer
ISA/US		M. Wilczewski M. Wilczewski

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
Y	JP,A, 57-102229 (Matsushita) 25 June 1982 (See Abstract)	1-20
A	JP,A, 57-187936 (Mizutani) 18 November 1982	
A	JP,A, 59-215728 (Yamazaki) 05 December 1984	
Y	JP,A, 60-37736 (Arikado) 27 February 1985 (See Abstract)	1-20
A	Zehner, D.M. and C.W. White; "Surface Studies Of Laser Annealed Semiconductors", in <u>Laser-Solid Interactions and Transient Thermal Processing Of Materials</u> , J. Narayan, W.L. Brown, R.A. Lemons, Eds., Matls. Res. Soc. Symp., Vol. 13, Elsevier Science Publishing Co., Inc., 1983, pp. 317-328.	
A	Zehner, D.M. et al., "Silicon Surface Structure and Surface Impurities After Pulsed Laser Annealing" in <u>Laser and Electron Beam Processing Of Materials</u> , C.W. White and P.S. Peercy, Eds., Academic Press, Inc., 1980, pp. 201-207.	

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

A	US,A, 4,680,616 (Delahoy et al) 14 July 1987
A,P	US,A, 4,782,029 (Takemura et al) 01 November 1988
A	JP,A, 56-7439 (Hayafuji et al) 26 January 1981
A	JP,A, 57-76846 (Itoga et al) 14 May 1982

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE ¹

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers _____, because they relate to subject matter ¹² not required to be searched by this Authority, namely:

2. ☐ Claim numbers _____, because they relate to parts of the International application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out ¹³, specifically:

3. ☐ Claim numbers _____, because they are dependent claims not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. ☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING ²

This International Searching Authority found multiple inventions in this international application as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the International application.

2. ☐ As only some of the required additional search fees were timely paid by the applicant, this International search report covers only those claims of the International application for which fees were paid, specifically claims:

3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

☐ The additional search fees were accompanied by applicant's protest.

☐ No protest accompanied the payment of additional search fees.