A method using atomic hydrogen for removing carbon contamination from optical surfaces. The method is particularly useful for removing carbon and hydrocarbon contamination in-situ from the surface of the multilayer optics used for extreme ultraviolet lithography (EUVL) without degrading the quality of the optical surface. Atomic hydrogen at pressures in the range of about $10^{-3}$ and $10^{-4}$ Torr without the potentially detrimental heating of the optic is used to provide cleaning rates of about 6-60 Å/hr.
Fig. 1

Water cooled thermal shield

Bechical Power

Current

Hot Filament

H₂

H⁺

EUV Optic

Water

Hydrogen
Atomic Hydrogen Cleaning of Photoresist

Fig. 2a

Atomic Hydrogen Cleaning of Sputtered Carbon

Fig. 2b
Auger Depth Profile of Sample Si-Capped Mo/Si optic
Exposed to 9.3 E-4 T Atomic H2 for 20hrs

Fig. 5a

Fig. 5b
Auger Depth Profile of 23Å Ru/20.7Å B4C/20.7Å Si/MLM Masked Area

Exposed to Atomic H2 at 9.3E-4 T for 20hrs

Fig. 6a

Fig. 6b
METHOD FOR REMOVING CARBON CONTAMINATION FROM OPTIC SURFACES

STATEMENT OF GOVERNMENT INTEREST

[0001] This invention was made with Government support under contract no. DE-AC04-94AL85000 awarded by the U.S. Department of Energy to Sandia Corporation. The Government has certain rights in the invention.

CROSS-REFERENCE TO RELATED APPLICATIONS

[0002] Not applicable.

FIELD OF THE INVENTION

[0003] This invention pertains to an in-situ method for removing carbon contamination from optical surfaces and particularly for removing carbon contamination from the surface of multilayer optics used for extreme ultraviolet lithography (EUVL). The method is directed to the use of atomic hydrogen at pressures significantly greater than those used conventionally and without heating of the optic.

BACKGROUND OF THE INVENTION

[0004] Degradation of reflectivity has long been a problem associated with optical components (mirrors, gratings, etc.) exposed to high energy radiation. In such systems, exposed optical surfaces develop carbaceous deposits as a result of photoemission-induced cracking of hydrocarbons adsorbed on these surfaces. This layer of contamination absorbs incident radiation and reduces the reflectivity of optical surfaces. Carbon contamination is of special concern in extreme ultraviolet lithography (EUVL) since carbon effectively absorbs radiation at 13.4 nm, the wavelength most commonly employed in this technology. For EUVL to be a viable next generation lithography technique, optics must be capable of operating for extended periods of time (years) with less than 2% loss in absolute reflectivity. To attain this objective, carbon contamination must be limited to a layer of less than about 20 Å and preferably in the range of 5-10 Å.

[0005] Strategies for cleaning EUVL optical surfaces should have the following attributes:

[0006] 1) The cleaning method should operate in-situ since ex-situ cleaning requires optic removal and undesirable and possibly excessive tool downtime.

[0007] 2) Since there are stringent requirements on the maximum temperature and temperature gradients in the EUVL tool and components contained therein, in particular multilayer optics, cleaning processes that require significant heating can not be used; the cleaning process should operate effectively at a temperature as close to ambient as possible.

[0008] 3) The cleaning process should resuscitate contaminated optical surfaces by restoring reflectivity uniformly over the optic while, at the same time, maintaining surface and bulk optical and physical properties of the multilayer optics.

[0009] Techniques for carbon gassification are well known in the semiconductor processing industry. These methods include the use of plasma discharges or sources of neutral atomic particles at elevated temperatures and pressures (cf. U.S. Pat. No. 5,312,591 Method of Cleaning A Charged Beam Apparatus and Muiller et al., Cleaning of Carbon Contaminated Vacuum Ultra-violet Optics: Influence on Surface Roughness and Reflectivity, Rev. of Sci. Instrum., 65, 1428-1431, January 1992). While these methods have been shown to remove carbon and hydrocarbon contamination they are not amenable to cleaning of the multilayer thin film optics used for EUVL. Carbon contamination on the surface of EUV optics is expected to be highly nonuniform. Consequently, some regions of the optic surface can be exposed to the cleaning procedure for a longer period of time than others. Over exposure of the optic surface can result in adverse effects to the optic (overshoot risks). Remote radio frequency (RF) discharges used to produce oxygen species can be effective in removing carbon deposits but induce surface oxidation in the Si-capped Mo/Si reflective optics and erode the surface of Ru—B,C-capped Mo/Si optics used in EUVL. Both of these effects result in permanent loss in reflectivity of the optics. By way of example, the addition of 4 Å of an oxide film beyond the thin film interference levels (~17 Å) will cause a loss in absolute reflectivity of about 1%. While RF-hydrogen has been demonstrated to clean carbon contamination at room temperature, a small but significant loss in reflectivity from, as yet unknown causes, has been observed over exposure times as short as 3 hours. This loss is believed to be related to the diffusion and reaction of hydrogen ions produced by the RF-hydrogen process with the outer layers of Si-capped Mo/Si optics.

[0010] One challenge in EUVL is that optics will be buried under layers of surrounding hardware, such as mechanical frames and cabling, as well as mechanical devices used to perform and monitor the lithographic process. For reference, a state-of-the-art EUVL tool is described in U.S. Pat. No. 6,031,598 to Tichenor et al. Reactive gas phase species that encounter solid objects can be quenched prior to reaching the optic surfaces that are to be cleaned. The obscuring structures in the machine make it very difficult to direct reactive species from the tool perimeter, where they are generated, to the optics located in the interior of the machine. Moreover, the integration of an RF source with delicate electronics in an EUV lithographic tool presents additional challenges.

[0011] Atomic hydrogen cleaning has been effectively demonstrated in molecular epitaxy surface preparation of Si, GaAs and InP at pressures in the range of about 10^{-6} Torr. However, in all cases, both native oxide and hydrocarbon contamination are typically removed at temperatures of several hundred degrees Celsius (cf. Hirayama and Tatsumi, Si(111) Surface Cleaning Using Atomic Hydrogen and SiH4, Studied Using Reflection High-Enery Eelctron Diffraction, J. Appl. Phys., 66 (2), July 1989, and Sugaya and Kawai, Low-Temperature Cleaning of GaAs Substrate by Atomic Hydrogen Radiation, Japan J. Appl. Phys., 30 (3A), March 1991, Akatsu et al., GaAs Wafer Bonding by Atomic Hydrogen Surface Cleaning, J. Appl. Phys., 86 (12), December 1999). Consequently, the art is in need of a method to generate reactive species inside the optic mounting assembly in a manner that limits adverse effects on the optics themselves.

SUMMARY OF THE INVENTION

[0012] Accordingly, the present invention is based, in part, on a process that provides for removal of carbon and
hydrocarbon contamination from optical surfaces with substantially no degradation of the properties of the optical surface. In particular, the invention provides a method for removing carbon and hydrocarbon contamination from the Si-capped and Ru–B,C-capped multilayer Mo/Si optics used for EUVL. The invention is particularly suited for photolithography systems with optic surfaces that are otherwise inaccessible unless the system is dismantled. Further, the invention provides for cleaning at near room temperature with the cleaning species being generated near the contaminated optical surfaces. Moreover, the process is compatible with the sensitive electronics generally found in an EUVL tool.

[0013] In one embodiment, the invention is directed to a method for cleaning contaminated optical surfaces that includes:

[0014] providing a vacuum chamber to house the contaminated surface; and
[0015] injecting atomic hydrogen at a pressure of between about 10⁻³ to 10⁻⁴ Torr into the vacuum chamber.

[0016] In another embodiment, a system for cleaning carbon contaminated optic surfaces that includes:

[0017] a housing defining a vacuum chamber in which a surface to be cleaned is located; and
[0018] a source of atomic hydrogen capable of injecting atomic hydrogen into the vacuum chamber, wherein the pressure of atomic hydrogen within the vacuum chamber is between about 10⁻³ to 10⁻⁴ Torr, and wherein the surface is at a temperature of less than about 50° C. throughout the cleaning process.

BRIEF DESCRIPTION OF THE DRAWINGS

[0019] FIG. 1 is a schematic illustration of an atomic hydrogen source.

[0020] FIGS. 2a and 2b show the etch rate dependence of a photoresist coated surface (2a) and a sputtered carbon coating (2b) on hydrogen pressure.

[0021] FIGS. 3a and 3b are Auger depth profiles of a sputtered carbon-coated silicon surface before exposure to atomic hydrogen (3a) and after a 5-hr exposure (3b).

[0022] FIGS. 4a and 4b show Auger analyses of a silicon surface of a Mo/Si multilayer optic prior to exposure to atomic hydrogen (4a) and after a 3-hr exposure (4b).

[0023] FIGS. 5a and 5b show Auger analysis of a Si-capped Mo/Si optic prior to (5a) and following (5b) exposure to atomic hydrogen for 20 hours.

[0024] FIGS. 6a and 6b show Auger analysis of a Ru-capped Mo/Si optic prior to (6a) and following (6b) exposure to atomic hydrogen for 20 hours.

DETAILED DESCRIPTION OF THE INVENTION

[0025] It is well known in the art that atomic hydrogen can be used to clean contaminated surfaces and particularly carbon contaminated surfaces. However, as discussed above prior art atomic cleaning methods employ elevated temperatures (typically >200° C.) and very low pressures (<10⁻⁵ to 10⁻⁶ Torr) in order to facilitate a greater percentage of hydrogen atoms reaching the contaminated surface. The dependence on elevated temperatures is an unacceptably rigorous condition for cleaning contaminated optical surfaces in an EUVL tool because of degradation of the optical properties of the surface. The present invention employs atomic hydrogen to clean optical surfaces but under much less rigorous conditions. The inventors have found that thick (>100 Å) layers of carbon and photoresist material (>1000 Å) can be removed from an optical surface by subjecting an optical surface coated with these materials to atomic hydrogen at pressures between about 10⁻³ to 10⁻⁴ Torr. Moreover, in contrast to prior atomic hydrogen cleaning methods, it is not necessary to heat the optics, which for the multilayer reflective optics used for EUVL prevents degradation of the optical properties by interdiffusion of the components of the multilayer structure. It has been found that optical surfaces coated with carbon contamination can be cleaned in about 3-5 hrs without any damage to the underlying multilayer surface. Finally, the method is particularly suited for photolithography systems with optic surfaces that are otherwise inaccessible unless the system is dismantled.

[0026] The experiments below are provided to illustrate and exemplify the invention and are not intended to be limiting. Modifications and variations may become apparent to those skilled in the art, however these modifications and variations come within the scope of the appended claims. Only the scope and content of the claims limit the invention.

[0027] Atomic hydrogen was produced by a source arranged in a configuration such as illustrated in FIG. 1. Hydrogen gas (H₂) was admitted through an inlet in the source and passed over a filament heated to a temperature of about 2400° C. to create atomic hydrogen (H) that flowed from the source and into a vacuum chamber the contmioned samples consisting of: 1) a Si wafer coated with about 1000 Å of photoresist, 2) a Si wafer coated with a 100 Å layer of sputtered carbon, 3) a bare Si-capped Mo/Si multilayer optic, and 4) a bare Ru–B,C-capped Mo/Si multilayer optic. These samples were placed about 8 inches downstream from an atomic hydrogen source. Following an exposure lasting from 3-5 hours the samples were removed from the vacuum chamber and the surfaces analyzed by Auger spectroscopy and reflectometry to determine their surface composition and reflectivity at an EUV wavelength of 13.4 nm. Because of the possibility that IR radiation emitted from the filament could be absorbed by the walls of the source causing the walls to heat up and, in turn, emit IR radiation which could irradiate the samples, the walls of the source were water cooled. Surfaces to be cleaned were placed far enough away from the atomic hydrogen source so that heating of the sample surface by IR radiation emitted by the atomic hydrogen source was negligible. In a typical EUVL tool the optics are water cooled further reducing the possibility of unwanted surface heating.

[0028] The cleaning rate was determined as a function of pressure. The results are shown in FIGS. 2a and 2b for cleaning photoresist (FIG. 2a) and sputtered carbon (FIG. 2b) from a coated surface. These data show that the rate of cleaning (etching) these surfaces reaches a maximum at between 10⁻³-10⁻⁴ Torr. In both cases rates of surface cleaning of from 6-60 Å/hr were observed. At the conclusion of the cleaning experiments, the temperatures of the samples was determined to be about 50° C., only slightly above
ambient (~22°C), and well below the 70°C limit for long-term stability of Mo/Si optics.

[0029] Referring now to FIG. 3, an Auger analysis of the surface of a silicon sample coated with sputtered carbon is shown in FIG. 3a. After exposure to atomic hydrogen at a pressure of about 9x10⁻⁴ Torr for about 4.5 hours, the sample was again analyzed by Auger depth profiling. As shown in FIG. 3b, the carbon coating is nearly gone resulting in a carbon etch rate of about 20 Å/hr.

[0030] EUV-based contamination of optical surfaces is not expected to be uniformly distributed over the optical surface. Consequently, bare portions of the optical surface can be exposed to atomic hydrogen for varying amounts of time. A series of experiments were undertaken to determine if any degradation in optical performance would be induced by direct exposure of the optical surface to atomic hydrogen.

[0031] A bare Si-capped Mo/Si multilayer optic was exposed to atomic hydrogen at a pressure of about 2x10⁻⁴ Torr for 3 hours. Prior to beginning the experiment an Auger sputter profile of the Si surface was taken (FIG. 4a). After the 3 hour exposure an Auger sputter profile of the Si surface was taken again (FIG. 4b). A comparison of these two Auger patterns shows a slight increase in surface silicon oxide (less than 3 Å). Reflectometry at 13.4 nm showed a peak reflectance of about 66.9±0.1% prior to exposure and 66.5±0.1% afterward. Within experimental error, the surface reflectivity was unchanged in spite of exposure to atomic hydrogen for 3 hours.

[0032] In order to explore in more detail the effects of exposure of an optic surface to atomic hydrogen, uncoated (i.e., lacking a carbon surface layer) multilayer optics having either a Si or Ru—B₃C capping layer were exposed to atomic hydrogen at a pressure of about 9x10⁻⁴ Torr for about 20 hrs. It should be noted that these exposure conditions is equivalent to about 40 cleaning cycles or the number of cleaning cycles that an optic would undergo over about 5-7 years, the designated life of the optic.

[0033] Results of Auger depth profiling of the exposed surfaces are shown in FIGS. 5 and 6. FIG. 5 shows the growth of a very thin silicon oxide film (~10 Å) on the Si surface. At-wavelength reflectometry at 13.4 nm shows a loss in absolute surface reflectivity on the order of about 1%. Comparison of FIGS. 6a and 6b shows that the composition of the Ru surface was substantially unchanged during the 20 hr. exposure to atomic hydrogen. At-wavelength reflectometry (13.4 nm) of these surfaces showed a loss in reflectivity of about 0.5%. These data show reflectivity losses well within the specification of 2% for an EUV tool. The small losses in reflectivity experienced by exposure of an uncoated multilayer optic to atomic hydrogen for extended periods of time are substantially less than seen with RF-discharge cleaning methods where losses in reflectivity of about 1% or greater are experienced for exposures less than 3 hrs.

[0034] In summary, atomic hydrogen has been shown to efficiently remove surface contamination (sputtered carbon and hydrocarbon material) from both the Si and Ru surfaces of multilayer optics with little adverse effect on the EUV reflectivity of the surfaces. In contrast to prior art atomic hydrogen cleaning methods, the cleaning rate disclosed here is most efficient at atomic hydrogen pressures of between 10⁻³ and 10⁻⁴ Torr. Moreover, prior art atomic hydrogen cleaning methods have required heating of the component being cleaned to several hundred degrees Celsius, such is not the case here. While the temperature of the optic being cleaned rose slightly (to ~50°C), presumably due to radiative heating by the atomic hydrogen source, no heating of the optics was found to be necessary for efficient cleaning. Furthermore, the cleaning method disclosed here has been found to produce negligible surface damage, even to uncoated surfaces, in contrast to prior cleaning methods.

We claim:

1. A method for removing contaminants from a surface, comprising:

   providing a vacuum chamber to house the contaminated surface; and

   injecting atomic hydrogen at a pressure of between about 10⁻³ and 10⁻⁴ Torr into the vacuum chamber.

2. The method of claim 1, wherein the contaminated surface is the surface of a multilayer optic.

3. The method of claim 2, wherein the multilayer optic is a Si-capped Mo/Si multilayer optic or a Ru—B₃C-capped Mo/Si multilayer optic.

4. A system for removing contaminants from a surface, comprising:

   a housing defining a vacuum chamber in which a surface to be cleaned is located; and

   a source of atomic hydrogen capable of injecting atomic hydrogen into the vacuum chamber, wherein pressure of atomic hydrogen within the vacuum chamber is between 10⁻³ to 10⁻⁴ Torr, and wherein the surface is at a temperature of less than about 50°C throughout the cleaning process.

5. The system of claim 4, wherein the surface is the surface of a multilayer optic.

6. The system of claim 5, wherein the multilayer optic is a Si-capped Mo/Si multilayer optic or a Ru—B₃C-capped Mo/Si multilayer optic.

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