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- (71) Applicant (for all designated States except US): **THE REGENTS OF THE UNIVERSITY OF CALIFORNIA** [US/US]; 1111 Franklin Street, Oakland, CA 94607-5200 (US).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): **BRITTEN, Jerald, A.** [US/US]; 5070 Morgan Territory Road, Clayton, CA 94517 (US). **NGUYEN, Hoang, T.** [US/US]; 2437 Robinson Circle, Livermore, CA 94550 (US).
- (74) Agent: **TAK, James, S.**; P.O. Box 808, L-703, Livermore, CA 94550 (US).
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(54) Title: METHOD FOR CLEANING DIFFRACTION GRATINGS

(57) Abstract: A method of cleaning a diffraction grating preferably includes exposing the grating surface to an aqueous base to remove an organic photoresist mask thereon; rinsing the grating surface with de-ionized water; oxidizing acid solution (such as Nanostrip™ or Nanostrip™ 2X) to remove metallic contaminants and residue organic compounds; rinsing the grating surface with de-ionized water; exposing the grating surface to an oxygen plasma ashing process using reactive oxygen species to oxidize and remove fluorinated hydrocarbon residue; exposing the grating surface again to an oxidizing acid solution to remove metallic contaminants and residue organic compounds; and rinsing the grating surface with de-ionized water.



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METHOD FOR CLEANING DIFFRACTION GRATINGS

I. FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0001] The United States Government has rights in this invention pursuant to Contract No. W-7405-ENG-48 between the United States Department of Energy and the University of California for the operation of Lawrence Livermore National Laboratory.

II. REFERENCE TO PRIOR APPLICATIONS

[0002] This application claims priority in provisional application filed on August 23, 2006, entitled "Method for Cleaning Diffraction Gratings" serial number 60/839,753, by Jerald A. Britten et al, and incorporated by reference herein.

III. BACKGROUND OF THE INVENTION

A. TECHNICAL FIELD

[0003] The present invention relates to methods of cleaning diffraction gratings, and more particularly to a method of cleaning diffraction gratings by exposure to a number of cleaning steps including exposure to aqueous base solutions, aqueous acid solutions, and an oxygen plasma, for the purpose of maximizing the laser damage resistance of the gratings.

B. DESCRIPTION OF THE RELATED ART

[0004] Diffraction gratings are an essential component of high-energy short-pulse laser systems. They act to expand the time-duration of seed pulses to enable propagation of these pulses through gain media for purposes of amplification, and then to re-compress the time duration of these pulses following amplification. As discussed in the article entitled, "Manufacture and Development of Multilayer Diffraction Gratings," Proc. of SPIE Vol. 5991, September 2005, incorporated by reference herein, multilayer dielectric (MLD) diffraction gratings are often preferred for such applications due to the

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high intrinsic laser damage thresholds of the materials comprising the MLD grating.

[0005] In order for such gratings to operate properly and optimally, however, it is important that the grating surface be completely clean and free from any contamination that can possibly absorb any small fraction of the incident light, as this absorption leads to multi-photon ionization, electronic avalanche breakdown and physical damage to the grating surface due to high laser intensities and the electric field enhancement effects of the grating surface inherent during the recompression process. The process of manufacturing gratings, however, can introduce a wide variety of surface contaminants, including, for example, organic photoresist material from the mask generation process, metals and fluoro-hydrocarbon deposits from the ion-beam etching process, and airborne organic and particulate contamination from all types of sources. It is the deposits from the ion beam etching steps that are typically the most troublesome to remove.

[0006] One known method for cleaning diffraction gratings involves exposing the grating to an oxygen plasma in a vacuum process. While this is effective in oxidizing and desorbing organic contamination, it does little to remove trace metallic contamination, for instance. Other cleaning methods are also known for cleaning mirrors, lenses, and other substantially planar optics subjected to high laser intensities, which employ mechanical means, such as ultrasonic, megasonic, or manual contact of the surface, even by polishing compounds, to mechanically remove contaminants. However, the submicron surface relief structures of diffraction gratings are extremely fragile and cannot survive such mechanical cleaning methods.

[0007] Therefore, it would be advantageous to provide a method for cleaning diffraction gratings involving a number of cleaning operations to remove all contamination from the surface of an MLD diffraction grating that are not all removable by a single cleaning process or chemistry.

IV. SUMMARY OF THE INVENTION

[0008] One aspect of the present invention includes a method of cleaning a diffraction grating comprising: exposing the grating surface to an oxidizing acid solution to remove metallic contaminants and residue organic compounds; rinsing the grating surface with de-ionized water; exposing the grating surface to an oxygen plasma ashing process using reactive oxygen species to oxidize and remove fluorinated hydrocarbon residue; exposing the grating surface again to an oxidizing acid solution to remove metallic contaminants and residue organic compounds; and rinsing the grating surface with de-ionized water.

V. DETAILED DESCRIPTION

[0009] Generally, single-step cleaning for MLD diffraction gratings for high laser damage resistance is not possible due to the several types of contamination present on the surface that are not removed by any one process. A number of cleaning operations are necessary to remove all contamination from the surface of an MLD diffraction grating. The exact details of the cleaning steps can be influenced by the materials comprising the diffraction grating, and also be influenced by the manner in which these materials have been deposited during the multilayer coating process.

[0010] Applicants have demonstrated the following process to be effective for the cleaning of MLD gratings consisting of alternating layers of, for example, $\text{HfO}_2/\text{SiO}_2$ with a grating etched into the top SiO_2 layer:

[0011] (1) Exposure of a grating surface to aqueous base (5% NaOH solution or commercial RS6 solution available from Cyantek Corporation of Fremont, California), at room temperature in a gentle agitation, e.g. by flowing the aqueous base thereon. Preferably, this is performed for approximately 5 minutes. This removes the bulk of the organic photoresist mask. This step is immediately followed by extensive rinsing with de-ionized (DI) water, and preferably ultrapure DI water.

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[0012] (2) Exposure of grating surface to aqueous oxidizing acid solution, preferably aqueous oxidizing sulfuric acid solution such as for example Nanostrip™ or Nanostrip™ 2X solution, commercially available from Cyantek Corporation, self-heated by periodic addition of water to 50-70 C, or at room temperature, in a gentle agitation (e.g. flow) process. This is preferably performed for approximately 60 minutes. This removes metallic contaminants and residue organic compounds. Alternatively, a point-of-use oxidizing acid solution, such as for example 'Piranha' solution, can be used to similar effect, although not at room temperature. This step is immediately followed by extensive rinsing with ultrapure DI water. It is appreciated that Piranha solution is a mixture of a strong acid (e.g. sulfuric acid, H_2SO_4) and a strong oxidizing agent (e.g. hydrogen peroxide, H_2O_2) which produces an extremely energetic solution. However, Piranha solution must be prepared immediately before use, has a very limited shelf life, and cannot be stored in normal closed containers due to an explosive pressure buildup caused by the gradual loss of hydrogen peroxide gas, ergo "point of use."

[0013] (3) Optionally, exposure of grating surface to a weak tetramethyl ammonium hydroxide solution to neutralize any remaining acidic residue on the surface, flowed by extensive rinsing with ultrapure DI water. This is performed prior to the next step.

[0014] (4) Exposure of grating surface to an oxygen plasma "ashing" process using reactive oxygen species generated by RF excitation of an oxygen flow in a vacuum chamber for a period of several hours. This process oxidizes and removes fluorinated hydrocarbon residue.

[0015] (5) Exposure of grating surface again to aqueous oxidizing acid solution, (preferably Nanostrip™ or Nanostrip™ 2X solution), self heated by periodic addition of water to 50-70 C, or at room temperature, in a gentle agitation (e.g. flow) process for approximately 60 minutes. This removes metallic contaminants possibly introduced by the ashing process. This step is immediately followed by extensive rinsing with ultrapure DI water.

[0016] The above process can be modified as necessary due to the incompatibility of certain MLD coating materials to certain chemistries. For example, if an Al_2O_3 etch-stop layer is incorporated into the MLD stack, treatment with aqueous base or hot acid is not possible due to dissolution of this layer. The cleaning process is modified by removing the first step (i.e. exposure to aqueous base) and changing steps (2) and (5) to room-temperature Nanostrip™ solution for a longer period of time greater than 60 minutes.

[0017] While particular operational sequences, materials, temperatures, parameters, and particular embodiments have been described and or illustrated, such are not intended to be limiting. Modifications and changes may become apparent to those skilled in the art, and it is intended that the invention be limited only by the scope of the appended claims.

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We claim:

1. A method of cleaning a diffraction grating comprising:
 - exposing the grating surface to an oxidizing acid solution to remove metallic contaminants and residue organic compounds;
 - rinsing the grating surface with de-ionized water;
 - exposing the grating surface to an oxygen plasma ashing process using reactive oxygen species to oxidize and remove fluorinated hydrocarbon residue;
 - exposing the grating surface again to an oxidizing acid solution to remove metallic contaminants and residue organic compounds; and
 - rinsing the grating surface with de-ionized water.
2. The method of claim 1, further comprising:
 - prior to performing the first exposure of the grating surface to an oxidizing acid solution, performing the steps of: exposing a grating surface to an aqueous base to remove an organic photoresist mask thereon, and rinsing the grating surface with de-ionized water.
3. The method of claim 2,
 - wherein the aqueous base is at room temperature.
4. The method of claim 2,
 - wherein during the exposure of the grating surface to the aqueous base, the aqueous base is agitated for about 5 minutes.
5. The method of claim 2,
 - wherein the aqueous base is selected from the group consisting of 5% NaOH solution and RS6 solution.
6. The method of claim 1, further comprising:

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prior to exposing the grating surface to the oxygen plasma ashing process, performing the steps of: exposing the grating surface to a weak tetramethyl ammonium hydroxide solution to neutralize any remaining acidic residue on the grating surface; and rinsing the grating surface with de-ionized water.

7. The method of claim 1,
wherein during at least one of the two exposures of the grating surface to the oxidizing acid solution, the oxidizing acid solution is agitated for about 60 minutes.
8. The method of claim 1,
wherein the oxidizing acid solution used in at least one of the two exposures of the grating surface to oxidizing acid solution, is an oxidizing sulfuric acid solution.
9. The method of claim 8,
wherein the oxidizing sulfuric acid solution is selected from the group consisting of Nanostrip™ solution and Nanostrip™ 2X solution.
10. The method of claim 8,
wherein the oxidizing sulfuric acid solution is self heated to 50-70 C by periodic addition of water.
11. The method of claim 8,
wherein the oxidizing sulfuric acid solution is at room temperature.
12. The method of claim 1,
wherein the oxidizing acid solution used is at least one of the two exposures of the grating surface to oxidizing acid solution, is a point-of-use oxidizing acid solution.

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13. The method of claim 12,
wherein the point-of-use oxidizing acid solution is Piranha solution.
14. The method of claim 1,
wherein the reactive oxygen species is generated by RF excitation of an oxygen flow in a vacuum chamber.
15. The method of claim 1,
wherein the diffraction grating is a multilayer dielectric (MLD) diffraction grating comprising alternating layers with a grating etched into a top layer.