METHODS OF LASER PROCESSING PHOTORESIST IN A GASEOUS ENVIRONMENT

FIELD

[0001] The present disclosure relates to photoresist processing, and in particular relates to systems and methods for processing a photoresist using laser processing and a gaseous environment to improve photoresist properties.

BACKGROUND

[0002] Photoresist is a photosensitive material used in semiconductor manufacturing in connection with forming small features in silicon in the process of forming a semiconductor device. As used in photolithography, a silicon wafer is coated with photoresist and placed in the photolithography tool. The particular pattern to be formed in the silicon wafer is embodied in a mask and the mask illuminated. The mask image is projected onto the photoresist, which is sensitive to the wavelength of illumination. The photoresist is then developed so that exposed portions of the photoresist are removed (for "positive" photoresist), leaving a copy of the mask pattern in the photoresist. The patterned photoresist is then etched, which transfers the pattern into the silicon wafer or other material under the photoresist.

[0003] Ideally, the photoresist pattern is binary in nature, having perfectly square sidewalls. Moreover, the ideal photoresist is able to replicate the mask image with perfect fidelity and serves as a perfect etch barrier. In practice, photoresist has a limited sensitivity, has some degree of line-edge roughness (LER) and is an imperfect etch barrier.

[0004] Efforts have been made to improve photoresist sensitivity, reduce LER and increase the etch resistance. In one case, sequential infiltration synthesis (SIS) is performed using trimethyl aluminum and water at temperatures of less than 100°C for several minutes to increase etch resistance and reduce LER. This process is described in the publication by Tseng et al., "Enhanced polymeric lithography resists via sequential infiltration synthesis," J. Mater. Chem., **21**, 2011 pp. 11722-25 (also cited as DOI: 10.1039/c1jm12461g).

[0005] Unfortunately, the several minutes it takes to carry out this process reduces wafer throughput at the manufacturing line.

SUMMARY

[0006] An aspect of the disclosure is a method of improving on a patterned product wafer at least one of an etch resistance and a line-edge roughness of a photoresist layer having a surface. The method includes: a) exposing the photoresist layer to at least one first process gas selected from the group consisting of trimethyl aluminum ($Al_2(CH_3)_6$) gas, titanium tetrachloride ($TiCL_4$) gas and diethyl zinc ($(C_2H_5)_2Zn$) gas; b) laser irradiating the photoresist layer and the first process gas to cause the first process gas to infuse into the photoresist layer, wherein the surface of the photoresist layer is raised to a temperature of between 300°C and 500°C with a temperature uniformity of +/– 5°C; c) removing remaining first process gas from a vicinity of the photoresist layer; d) exposing the photoresist layer to a second process gas comprising H_20; and e) laser irradiating the photoresist layer and second process gas to cause the H_2O to infuse into the photoresist layer, wherein the surface of the photoresist layer is raised to a temperature of between 300°C and 500°C with a temperature uniformity of +/– 5°C.

[0007] Another aspect of the disclosure is the method described above, wherein the laser irradiating includes scanning a laser beam over the surface of the photoresist layer.

[0008] Another aspect of the disclosure is the method described above, wherein the scanning includes either moving the laser beam, moving the patterned product wafer or moving both the laser beam and the patterned product wafer.

[0009] Another aspect of the disclosure is the method described above, wherein the laser beam forms a line image at the surface of the photoresist layer.

[0010] Another aspect of the disclosure is the method described above, wherein the line image has a dwell time τ in the range 1 ms $\leq \tau \leq$ 100 ms.

[0011] Another aspect of the disclosure is the method described above, wherein the line image has a width W in the range 0.2 mm $\leq$ W $\leq$ 2 mm and a length L in the range 10 mm $\leq$ L $\leq$ 100 mm.

[0012] Another aspect of the disclosure is the method described above, wherein the line image has a scan speed v_s in the range 20 mm/s $\leq v_s \leq$ 5,000 mm/s.

[0013] Another aspect of the disclosure is the method described above, wherein the laser beam has a power density P in the range 50 watts/cm^2 ≤ P ≤ 150 watts/cm^2.

[0014] Another aspect of the disclosure is the method described above, wherein the patterned product wafer is maintained in an interior of a process chamber.

[0015] Another aspect of the disclosure is the method described above, further comprising etching the processed patterned product wafer.

[0016] Another aspect of the disclosure is the method described above, wherein steps a) through e) are carried out over the entire wafer in a wafer process time of between 30 seconds and 120 seconds.

[0017] Another aspect of the disclosure is the method described above, wherein steps a) through e) are repeated one or more times, with an additional step of removing the second process gas from the vicinity of the photoresist layer after each step e).

[0018] Another aspect of the disclosure is the method described above, wherein the product wafer resides within a process chamber interior, and wherein removing the first process gas from the vicinity of the photoresist layer includes at least one of evacuation of the first process gas from the process chamber interior and purging the process chamber interior with an inert gas.

[0019] Another aspect of the disclosure is a method of processing a product wafer residing in an interior of a process chamber and having a patterned photoresist layer with a surface to improve at least one of an etch resistance and a line-edge roughness. The method includes: a) exposing the surface of the patterned photoresist layer to a first molecular process gas; b) scanning a laser beam over the surface of the patterned photoresist layer to cause infusion of molecules of the first molecular process gas into the patterned photoresist layer, wherein the surface of patterned photoresist layer is raised to a temperature of between 300°C and 500°C with a temperature uniformity of +/– 5°C; c) removing remaining first molecular process gas from the interior of process chamber; d) exposing the patterned photoresist layer to a second molecular process gas and repeating step b) for the second molecular process gas; and wherein the first molecular process gas is at least one selected from the group consisting of trimethyl aluminum ($Al_2(CH_3)_6$) gas,

titanium tetrachloride ($TiCL_4$) gas and diethyl zinc ($(C_2H_5)_2Zn$) gas, and the second molecular process gas comprises H_2O.

[0020] Another aspect of the disclosure is the method described above, wherein the laser beam forms a line image at the surface of patterned photoresist layer, and wherein the line image has a dwell time τ in the range 1 ms $\leq \tau \leq$ 100 ms.

[0021] Another aspect of the disclosure is the method described above, wherein the line image has a width W in the range 0.2 mm $\leq$ W $\leq$ 2 mm and a length L in the range 10 mm $\leq$ L $\leq$ 100 mm.

[0022] Another aspect of the disclosure is the method described above, wherein the line image has a scan speed v_s in the range 20 mm/s $\leq v_s \leq$ 5,000 mm/s.

[0023] Another aspect of the disclosure is the method described above, wherein the laser beam has a power density P in the range 50 watts/cm^2 $\leq$ P $\leq$ 150 watts/cm^2.

[0024] Another aspect of the disclosure is the method described above, further comprising etching the processed patterned product wafer.

[0025] Another aspect of the disclosure is the method described above, wherein steps a) through d) are carried out over the entire wafer in a wafer process time of between 30 seconds and 120 seconds.

[0026] Another aspect of the disclosure is the method described above, wherein removing the first molecular process gas from the interior of the process chamber includes at least one of evacuation of the first molecular process gas from the interior of process chamber and purging the interior of the process chamber with an inert gas.

[0027] Another aspect of the disclosure is a method of processing a product wafer residing in an interior of a process chamber and having a patterned photoresist layer having a surface to improve at least one of an etch resistance and a line-edge roughness. The method includes: a) sequentially introducing first and second molecular process gases to the interior of the process chamber, including removing the first or second molecular process gas from the interior of the process chamber prior to introducing the other of the first or second molecular process gas; b) laser scanning the surface of the patterned photoresist layer for each of the first and second molecular gases to cause the sequential infusion of the

first and second molecular gases into the patterned photoresist layer; and c) repeating steps a) and b) multiple times, wherein the first molecular gas is at least one selected from the group consisting of trimethyl aluminum ($Al_2(CH_3)_6$), titanium tetrachloride ($TiCL_4$) and diethyl zinc $(C_2H_5)_2Zn$), and the second molecular gas comprises water vapor.

[0028] Another aspect of the disclosure is the method described above, wherein the laser scans are performed using a laser beam that forms a line image, and wherein the line image has a dwell time τ in the range 1 ms $\leq \tau \leq$ 100 ms.

[0029] Another aspect of the disclosure is the method described above, wherein the line image has a width W in the range 0.2 mm $\leq$ W $\leq$ 2 mm and a length L in the range 10 mm $\leq$ L $\leq$ 100 mm.

[0030] Another aspect of the disclosure is the method described above, wherein the line image has a scan speed v_s in the range 20 mm/s $\leq v_s \leq$ 5,000 mm/s.

[0031] Another aspect of the disclosure is the method described above, wherein the laser beam has a power density P in the range 50 watts/cm^2 $\leq$ P $\leq$ 150 watts/cm^2.

[0032] Another aspect of the disclosure is the method described above, wherein removing the first or second molecular process gas from the interior of the process chamber includes at least one of: i) evacuation of the first or second molecular process gas from the interior of process chamber and ii) purging the interior of the process chamber with an inert gas.

[0033] Another aspect of the disclosure is a method of processing a product wafer residing in an interior of a process chamber and having a patterned photoresist layer having a surface to improve at least one of an etch resistance and a line-edge roughness. The method includes: a) exposing the surface of the patterned photoresist layer to a first process gas comprising molecules, wherein the first process gas molecules are at least one selected from the group of molecules consisting of trimethyl aluminum ($Al_2(CH_3)_6$) gas, titanium tetrachloride ($TiCL_4$) gas and diethyl zinc ($(C_2H_5)_2Zn$) gas; and b) scanning a laser beam over the surface of the patterned photoresist layer to cause infusion of the molecules of the first process gas into the patterned photoresist layer, wherein the surface of patterned photoresist layer is raised to a temperature of between 300°C and 500°C with a temperature uniformity of +/– 5°C.

[0034] Another aspect of the disclosure is the method described above, further comprising after step b): c) removing the first process gas from the interior of the process chamber; d) exposing the patterned photoresist layer to a second process gas containing H_2O molecules; and e) scanning the laser beam over the surface of the patterned photoresist layer to cause infusion of the H_2O molecules into the patterned photoresist layer.

[0035] Another aspect of the disclosure is the method described above, wherein removing the first process gas from the interior of the process chamber includes at least one of: i) evacuation of the first or second molecular process gas from the interior of the process chamber and ii) purging the interior of the process chamber with an inert gas.

[0036] Another aspect of the disclosure is the method described above, wherein scanning laser beam forms a line image having a dwell time τ in the range 1 ms $\leq \tau \leq$ 100 ms.

[0037] Another aspect of the disclosure is the method described above, wherein the line image has a width W in the range 0.2 mm $\leq$ W $\leq$ 2 mm, a length L in the range 10 mm $\leq$ L $\leq$ 100 mm, a scan speed v_s in the range 20 mm/s $\leq v_s \leq$ 5,000 mm/s, and a power density P in the range 50 watts/cm^2 $\leq$ P $\leq$ 150 watts/cm^2.

[0038] Another aspect of the disclosure is the method described above, wherein steps a) and b) are carried out over the entire product wafer in a wafer process time of between 30 seconds and 120 seconds.

[0039] Additional features and advantages will be set forth in the Detailed Description that follows, and in part will be readily apparent to those skilled in the art from the description or recognized by practicing the embodiments as described in the written description and claims hereof, as well as the appended drawings. It is to be understood that both the foregoing general description and the following Detailed Description are merely exemplary and are intended to provide an overview or framework for understanding the nature and character of the claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0040] The accompanying drawings are included to provide a further understanding and are incorporated into and constitute a part of this specification. The drawings illustrate one

or more embodiment(s) and together with the Detailed Description serve to explain the principles and operation of the various embodiments. As such, the disclosure will become more fully understood from the following Detailed Description, taken in conjunction with the accompanying Figures, in which:

[0041] FIG. 1 is a cross-sectional view of an example product wafer that includes a silicon substrate coated with a photoresist layer;

[0042] FIG. 2 is a top-down view of the product wafer of FIG. 1 and shows how the product wafer includes exposure fields and patterns with each exposure field;

[0043] FIG. 3 is a schematic diagram of an example laser processing system used to carry out the methods of processing the patterned product wafer to improve at least one of the etch resistance and LER;

[0044] FIG. 4 is an elevated view of an example laser beam that forms a line image at the surface of the photoresist layer having a width W and a length L;

[0045] FIG. 5 is a plan view of the photoresist layer of the patterned product wafer undergoing laser scanning during one of the process steps; and

[0046] FIG. 6 is similar to FIG. 3 and shows an alternate embodiment of the process chamber in the form of a microchamber.

DETAILED DESCRIPTION

[0047] Reference is now made in detail to various embodiments of the disclosure, examples of which are illustrated in the accompanying drawings. Whenever possible, the same or like reference numbers and symbols are used throughout the drawings to refer to the same or like parts. The drawings are not necessarily to scale, and one skilled in the art will recognize where the drawings have been simplified to illustrate the key aspects of the disclosure.

[0048] The claims as set forth below are incorporated into and constitute part of this Detailed Description.

[0049] The entire disclosure of any publication or patent document mentioned herein is incorporated by reference.

[0050] Cartesian coordinates are shown in some of the Figures for the sake of reference and are not intended to be limiting as to direction or orientation.

[0051] FIG. 1 is a cross-sectional view and FIG. 2 is a top-down view of an example product wafer 10. The product wafer 10 includes a silicon substrate 20 having a top surface 22. The top surface 22 of substrate 20 is coated with a layer of photoresist 30 that has a top surface 32 and a thickness TH. With reference to FIG. 2, the product wafer 10 includes an array of exposure fields ("fields") 40 that is formed by the photolithographic exposure of photoresist 30 on a field-by-field or multiple-field basis. In an example, the exposure fields 40 comprise subregions that define the boundaries for subsequent integrated circuit (IC) chips 44 (first close-up inset) that are formed when the fabrication of product wafer 10 is completed. The product wafer 10 as shown represents a semiconductor wafer during the IC fabrication process.

[0052] The photoresist 30 records in each field 40 an image of the pattern features on a photolithography reticle imaged in the layer of photoresist 30 using a photolithographic imaging system or "tool," as it is often referred to in the industry. An example photolithography tool is described for example in U.S. Patent No. 6,879,383. Thus, product wafer 10 is said to be "exposed" when all fields 40 are formed.

[0053] The exposed product wafer 10 is then subjected to a develop process that removes the unexposed photoresist 30 (in the case of "positive" photoresist). The result is that each field 40 now includes the same three-dimensional photoresist pattern 50, as shown in the second close-up inset of FIG. 1. The product wafer 10 at this stage of the process can be referred to as a "patterned product wafer."

[0054] In the usual next step, the patterned product wafer 10 is subjected to an etching process that etches the photoresist pattern 50 into the underlying silicon substrate 20. This is accomplished by photoresist pattern 50 serving as an etch-stopping structure.

[0055] As noted above, the photoresist 30 has performance limitations relating to, among other things, line edge roughness (LER) and etch resistance.

[0056] FIG. 3 is a schematic cross-sectional view of an example laser processing system 100 for processing the patterned product wafer 10 to improve the performance of

photoresist 30 with respect to at least one of LER and etch resistance, as compared to not processing the patterned product wafer 10.

[0057] The laser processing system 100 includes a process chamber 110 that has an interior 112 sized to accommodate the patterned product wafer 10. The process chamber 110 has a top wall 114 that includes a window 116 that is transparent to a select wavelength range $\Delta\lambda$ that includes a process wavelength λ, as discussed below. In an example, the window 116 is made of fused silica. The laser processing system 100 resides in an ambient environment 104. The process chamber 110 is configured to provide a controlled environment in the interior 112 of process chamber 110 for processing the photoresist 30, as described below.

[0058] The patterned product wafer 10 is supported in the interior 112 of process chamber 110 by a wafer stage 130. In an example, the wafer stage 130 is movable in the x, y and z directions and can also be rotated about the x, y and z axes as needed. The wafer stage 130 is operably connected to a wafer-stage driver 134.

[0059] The laser processing system 100 also includes at least one process-gas source 150A and 150B fluidly connected to the interior 112 of process chamber 110 and that emits at least one process gas 152A and 152B. In an example, the at least one process gas 152A and 152B is a molecular gas. In the example laser processing system 100 of FIG. 3, first and second process-gas sources 150A and 150B that emit first and second process gasses 152A and 152B are shown by way of example. In an example, the first process gas 152A is a molecular gas that is at least one selected from the group comprising or consisting of trimethyl aluminum ($Al_2(CH_3)_6$), titanium tetrachloride ($TiCL_4$) and diethyl zinc ($(C_2H_5)_2Zn$). Also in an example embodiment, the second process gas 152B comprises water vapor, i.e., H_2O gas. In an example, the water vapor can be a constituent of air or of another gas rather than being pure water vapor.

[0060] The laser processing system 100 also includes a vacuum system 160 fluidly connected to the interior 112 of process chamber 110. The vacuum system 160 is used to remove any gasses from the interior 112 of process chamber 110 at select times during the processing of patterned product wafer 10, as described below.

[0061] The laser processing system 100 also includes an inert gas source 170 fluidly connected to the interior 112 of process chamber 110 and that can provide an inert gas 172 to perform a purge of the first process gas 152A or the second process gas 152B. In an example, the inert gas 172 is nitrogen. This serves to remove the process gas 152A or 152B from the vicinity of layer of photoresist 30 so that the process gas 152A or 152B is no longer available to react with the layer of photoresist 30.

[0062] The laser processing system 100 also includes a laser system 180 that generates a laser beam 182 having the process wavelength λ. In an example, the laser beam 182 can scan, as illustrated by arrow AR. The laser processing system 100 may include beam-conditioning optics (not shown), which may include beam-scanning elements and components (e.g., a scanning mirror).

[0063] FIG. 4 is an elevated view of an example line image 182L formed by the laser beam 182 when the laser beam 182 intersects the top surface 32 of layer of photoresist 30, as explained below. The line image 182L has a width W and a length L. The width W and length L of line image 182L depends on the illumination angle of incidence α measured relative to the normal N of the top surface 32 of layer of photoresist 30.

[0064] In an example, the laser system 180 generates the laser beam 182 having the following parameters, as summarized in Table 1.

Table 1 - Example laser-beam parameters

Parameter	Range
Beam width W	0.1 mm to 2 mm
Beam length L	10 mm to 100 mm
Dwell time τ	1 to 100 milliseconds (ms)
Process wavelength λ	300 nm to 1,200 nm
Power density P	50 to 150 watts/mm^2
Scan speed v_s	10 to 5,000 mm/s

[0065] In Table 1, the dwell time τ is the length of time line image 182L resides over a point on the top surface 32 of layer of photoresist 30. The scan speed v_S is the speed at which the line image 182L moves over the top surface 32 of layer of photoresist 30. FIG. 5 is a top-down view of the patterned product wafer 10 illustrating how the line image 182L moves over the top surface 32 of layer of photoresist 30. The movement of line image 182L relative to the top surface 32 of layer of photoresist 30 can be effectuated by moving the (scanning) laser beam 182, by moving the wafer stage 130 or by a combination of these movements. In an example, the scanning of laser beam 182 is in a back-and-forth manner, e.g., in a boustrophedonic manner or raster-scan manner.

[0066] The laser processing system 100 also includes a controller 200 operably connected to at least one of the process-gas sources 150A and 150B, to the wafer-stage driver 134, to the vacuum system 160, to the inert gas source 170 and to the laser system 180 to control the overall operation of the laser processing system 100 in processing the patterned product wafer 10. In an example, the controller 200 is or includes a computer, such as a personal computer or workstation. The controller 200 preferably includes any of a number of commercially available microprocessors, a suitable bus architecture to connect the microprocessor to a memory device, such as a hard disk drive, and suitable input and output devices (e.g., a keyboard and a display, respectively). The controller 200 can be programmed via instructions (software) embodied in a computer-readable medium (e.g., memory, processor or both) that cause the controller 200 to carry out the various functions of laser processing system 100 to effectuate processing of the patterned product wafer 10.

[0067] In the operation of laser processing system 100 to process the patterned product wafer 10, in a first step, the vacuum system 160 is operated to remove ambient gas in the interior 112 of process chamber 110 to create an initial condition for initiating the process, e.g., wherein the interior 112 of process chamber 110 contains less than 100 parts per million (ppm) of oxygen. Once the initial condition is established, then in a second step, the first process gas 152A is introduced into the interior 112 of process chamber 110 where the first process gas 152A interfaces with the top surface 32 of layer of photoresist 30.

[0068] Next, in a third step, the laser beam 182 is scanned (e.g., raster scanned) over the patterned product wafer 10, i.e., the line image 182L is scanned over the top surface 32 of layer of photoresist 30. In an example, this laser-scanning operation raises the temperature

of photoresist 30 to between 300°C and 500°C within a temperature uniformity of +/– 5°C. This causes molecules of the first process gas 152A to infuse into the photoresist 30. For the example parameters set forth in Table 1, it can take from about 30 seconds to about 120 seconds to scan the entire patterned process wafer 10. This time period is referred to herein as the "wafer process time."

[0069] This part of the method or process is similar to an atomic layer deposition (ALD) process whereby monotomic layers of a material are deposited onto a surface and then reacted to affect the surface as well as a portion of the underlying volume. In the present case, the infusion of trimethyl aluminum has been shown to improve the etch resistance of photoresist 30. However, as discussed above, the prior-art process for performing the infusion is done slowly at low temperature. Here, the infusion into the volume of photoresist 30 is done in a matter of milliseconds.

[0070] It is noted here that the short dwell time τ of laser-beam line image 182L prevents the photoresist 30 from flowing so that the photoresist pattern 50 is maintained. The laser beam 182 thus serves to raise the surface temperature of photoresist 30 to selectively deposit ALD-type material onto the top surface 32 of layer of photoresist 30 or into the bulk of the photoresist 30.

[0071] Once laser-beam line image 182L is scanned over the top surface 32 of layer of photoresist 30 (see FIG. 5), then in a fourth step, the first process gas 152A that remains in the vicinity of layer of photoresist 30 is removed. This can be accomplished by evacuating the interior 112 of process chamber 110 using the vacuum system 160. Alternatively, or in combination with the vacuum evacuation, the fourth step may include activating inert gas source 170 and flushing the interior 112 of process chamber 110 with the inert gas 172.

[0072] Then, in a fifth step (which may be optional, depending on the type of first process gas 152A used), second process gas 152B is introduced into the interior 112 of process chamber 110. As noted above, in an example, the second process gas 152B is a molecular gas and comprises water vapor (H_2O).

[0073] Next, in a sixth step, the laser-beam line image 182L is scanned over the top surface 32 of layer of photoresist 30 to cause infusion of H_2O molecules into the layer of

photoresist 30. In a seventh step, the second process gas 152B is removed from the interior 112 of process chamber 110 in one of the manners described above.

[0074] Steps two through seven can be repeated as many times as is required to achieve the desired degree of improvement in one or both of LER and etch resistance.

[0075] In example embodiments, the following first and second process gases 152A and 152B can be used: 1) trimethyl aluminum and water vapor to infuse aluminum or sapphire, Al_2O_3; 2) titanium tetrachloride and water vapor to infuse Ti or TiO; and 3) diethyl zinc and water vapor to infuse zinc or ZnO.

[0076] The second process gas 152B in the form of water vapor is used to create the metal oxide. In an example, the infusion of the trimethyl aluminum, titanium tetrachloride or diethyl zinc into the photoresist 30 is performed without introducing the second process gas 152B to form an etch barrier.

[0077] FIG. 6 is similar to FIG. 3 and illustrates an alternative embodiment of the laser processing system 100 wherein the process chamber 110 is in the form of a microchamber, such as those disclosed in U.S. Patent No. 5,997,963, entitled "Microchamber" and U.S. Patent Application No. 13/690,132, entitled "Movable microchamber with gas curtain." The wafer stage 130 is shown supporting a chuck 132, which in turn supports the patterned product wafer 10. A platen 136 movably supports the movable wafer stage 130. The top wall 114 includes the window 116 sized to pass the laser beam 182. In an example, the laser beam 182 is incident upon the photoresist 30 at an angle other than normal incidence.

[0078] In an example, an air curtain 220 is employed to prevent ambient gas (such as oxygen) in the ambient environment 104 from entering the interior 112 of process chamber 110, which in an example is not otherwise sealed off from the ambient environment of process chamber 110. For a microchamber process chamber 110, the original gas residing in the interior 112 is pushed out by flooding the interior 112 with the particular process gas (i.e., the first or second process gas 152A or 152B). In an example, the inert gas 112 from the inert gas source 170 is used to flush out the original gas (e.g., air) or to flush out the process gas 152A or 152B between the process steps.

[0079] Once the patterned product wafer 10 is processed using one of the processes described above, it has at least one of improved etch resistance and, or the LER as

compared to a patterned product wafer 10 that has not been so processed. At this point, the processed patterned product wafer 10 can be subjected to a standard semiconductor manufacturing etch process along the way to forming semiconductor devices.

[0080] It will be apparent to those skilled in the art that various modifications to the preferred embodiments of the disclosure as described herein can be made without departing from the spirit or scope of the disclosure as defined in the appended claims. Thus, the disclosure covers the modifications and variations provided they come within the scope of the appended claims and the equivalents thereto.

What is claimed is:

1. A method of improving on a patterned product wafer at least one of an etch resistance and a line-edge roughness of a photoresist layer having a surface, comprising:

a) exposing the photoresist layer to at least one first process gas selected from the group consisting of trimethyl aluminum ($Al_2(CH_3)_6$) gas, titanium tetrachloride ($TiCL_4$) gas and diethyl zinc ($(C_2H_5)_2Zn$) gas;

b) laser irradiating the photoresist layer and the first process gas to cause the first process gas to infuse into the photoresist layer, wherein the surface of photoresist layer is raised to a temperature of between 300°C and 500°C with a temperature uniformity of +/– 5°C;

c) removing remaining first process gas from a vicinity of the photoresist layer;

d) exposing the photoresist layer to a second process gas comprising H_20; and

e) laser irradiating the photoresist layer and second process gas to cause the H_2O to infuse into the photoresist layer, wherein the surface of photoresist layer is raised to a temperature of between 300°C and 500°C with a temperature uniformity of +/– 5°C.

2. The method according to claim 1, wherein the laser irradiating includes scanning a laser beam over the surface of the photoresist layer.

3. The method according to claim 1, wherein the scanning includes either moving the laser beam, moving the patterned product wafer or moving both the laser beam and the patterned product wafer.

4. The method according to claim 2, wherein the laser beam forms a line image at the surface of photoresist layer.

5. The method according to claim 4, wherein the line image has a dwell time τ in the range $1\ ms \leq \tau \leq 100\ ms$.

6. The method according to claim 4, wherein the line image has a width W in the range 0.2 mm ≤ W ≤ 2 mm and a length L in the range 10 mm ≤ L ≤ 100 mm.

7. The method according to claim 4, wherein the line image has a scan speed v_s in the range 20 mm/s ≤ v_s ≤ 5,000 mm/s.

8. The method according to claim 2, wherein the laser beam has a power density P in the range 50 watts/cm^2 ≤ P ≤ 150 watts/cm^2.

9. The method according to claim 1, wherein the patterned product wafer is maintained in an interior of a process chamber.

10. The method according to claim 1, further comprising etching the processed patterned product wafer.

11. The method according to any of claims 1 through 10, wherein steps a) through e) are carried out over the entire wafer in a wafer process time of between 30 seconds and 120 seconds.

12. The method according to claim 1, wherein steps a) through e) are repeated one or more times, with an additional step of removing the second process gas from the vicinity of the photoresist layer after each step e).

13. The method according to claim 1, wherein the product wafer resides within a process chamber interior, and wherein removing the first process gas from the vicinity of the photoresist layer includes at least one of evacuating the first process gas from the process chamber interior and purging the process chamber interior with an inert gas.

14. A method of processing a product wafer residing in an interior of a process chamber and having a patterned photoresist layer with a surface to improve at least one of an etch resistance and a line-edge roughness, comprising:

a) exposing the surface of the patterned photoresist layer to a first molecular process gas;

b) scanning a laser beam over the surface of the patterned photoresist layer to cause infusion of molecules of the first molecular process gas into the patterned photoresist layer, wherein the surface of patterned photoresist layer is raised to a temperature of between 300°C and 500°C with a temperature uniformity of +/– 5°C;

c) removing remaining first molecular process gas from the interior of process chamber;

d) exposing the patterned photoresist layer to a second molecular process gas and repeating step b) for the second molecular process gas; and

wherein the first molecular process gas is at least one selected from the group consisting of trimethyl aluminum ($Al_2(CH_3)_6$) gas, titanium tetrachloride ($TiCL_4$) gas and diethyl zinc ($(C_2H_5)_2Zn$) gas, and the second molecular process gas comprises H_2O.

15. The method according to claim 14, wherein the laser beam forms a line image at the surface of patterned photoresist layer, and wherein the line image has a dwell time τ in the range 1 ms $\leq \tau \leq$ 100 ms.

16. The method according to claim 15, wherein the line image has a width W in the range 0.2 mm $\leq$ W $\leq$ 2 mm and a length L in the range 10 mm $\leq$ L $\leq$ 100 mm.

17. The method according to claim 15, wherein the line image has a scan speed v_s in the range 20 mm/s $\leq v_s \leq$ 5,000 mm/s.

18. The method according to claim 14, wherein the laser beam has a power density P in the range 50 watts/cm^2 $\leq$ P $\leq$ 150 watts/cm^2.

19. The method according to claim 14, further comprising etching the processed patterned product wafer.

20. The method according to claim 14, wherein steps a) through d) are carried out over the entire wafer in a wafer process time of between 30 seconds and 120 seconds.

21. The method according to claim 14, wherein removing the first molecular process gas from the interior of process chamber includes at least one of evacuation of the first molecular process gas from the interior of process chamber and purging the interior of process chamber with an inert gas.

22. A method of processing a product wafer residing in an interior of a process chamber and having a patterned photoresist layer having a surface to improve at least one of an etch resistance and a line-edge roughness, comprising:

a) sequentially introducing first and second molecular process gases to the interior of process chamber, including removing the first or second molecular process gas from the interior of process chamber prior to introducing the other of the first or second molecular process gas;

b) laser scanning the surface of patterned photoresist layer for each of the first and second molecular gases to cause the sequential infusion of the first and second molecular gases into the patterned photoresist layer; and

c) repeating steps a) and b) multiple times, wherein the first molecular gas is at least one selected from the group consisting of trimethyl aluminum ($Al_2(CH_3)_6$), titanium tetrachloride ($TiCL_4$) and diethyl zinc $(C_2H_5)_2Zn$), and the second molecular gas comprises water vapor.

23. The method according to claim 22, wherein the laser scans are performed using a laser beam that forms a line image, and wherein the line image has a dwell time τ in the range $1\ ms \leq \tau \leq 100\ ms$.

24. The method according to claim 23, wherein the line image has a width W in the range $0.2\ mm \leq W \leq 2\ mm$ and a length L in the range $10\ mm \leq L \leq 100\ mm$.

25. The method according to claim 23, wherein the line image has a scan speed v_s in the range 20 mm/s $\leq v_s \leq$ 5,000 mm/s.

26. The method according to claim 23, wherein the laser beam has a power density P in the range 50 watts/cm^2 $\leq$ P $\leq$ 150 watts/cm^2.

27. The method according to claim 23, wherein removing the first or second molecular process gas from the interior of process chamber includes at least one of: i) evacuation of the first or second molecular process gas from the interior of process chamber and ii) purging the interior of process chamber with an inert gas.

28. A method of processing a product wafer residing in an interior of a process chamber and having a patterned photoresist layer having a surface to improve at least one of an etch resistance and a line-edge roughness, comprising:

a) exposing the surface of the patterned photoresist layer to a first process gas comprising molecules, wherein the first process gas molecules are at least one selected from the group of molecules consisting of trimethyl aluminum ($Al_2(CH_3)_6$) gas, titanium tetrachloride ($TiCL_4$) gas and diethyl zinc ($(C_2H_5)_2Zn$) gas; and

b) scanning a laser beam over the surface of the patterned photoresist layer to cause infusion of the molecules of the first process gas into the patterned photoresist layer, wherein the surface of patterned photoresist layer is raised to a temperature of between 300°C and 500°C with a temperature uniformity of +/– 5°C.

29. The method according to claim 28, further comprising after step b):

c) removing the first process gas from the interior of process chamber;

d) exposing the patterned photoresist layer to a second process gas containing H_2O molecules; and

e) scanning the laser beam over the surface of the patterned photoresist layer to cause infusion of the H_2O molecules into the patterned photoresist layer.

30. The method according to claim 29, wherein removing the first process gas from the interior of process chamber includes at least one of: i) evacuating the first or second molecular process gas from the interior of process chamber and ii) purging the interior of process chamber with an inert gas.

31. The method according to claim 28, wherein scanning laser beam forms a line image having a dwell time τ in the range 1 ms $\leq \tau \leq$ 100 ms.

32. The method according to claim 31, wherein the line image has a width W in the range 0.2 mm $\leq$ W $\leq$ 2 mm, a length L in the range 10 mm $\leq$ L $\leq$ 100 mm, a scan speed v_s in the range 20 mm/s $\leq v_s \leq$ 5,000 mm/s, and a power density P in the range 50 watts/cm^2 $\leq$ P $\leq$ 150 watts/cm^2.

33. The method according to claim 28, wherein steps a) and b) are carried out over the entire product wafer in a wafer process time of between 30 seconds and 120 seconds.