

A Method of Generating A Pattern On A Substrate

FIELD OF INVENTION

5 The present invention relates broadly to a method of generating a pattern on a substrate, and to a pattern formed on a substrate using the method.

BACKGROUND

10 In a fabrication process of e.g. optical disc stampers, semiconductor devices, biosensors, microelectromechanical system (MEMS) devices, miniature electronics, micron-optical, and micromechanical devices, patterns of different shapes and sizes are usually generated on a surface of a substrate such as a silicon wafer through a process called lithography. Figures 1A to 1C illustrate a typical lithography process. An irradiating
15 resist 102 coated on a surface of a substrate 104 is irradiated with a laser beam (LB) or an electron beam (EB) 106 through a mask that carries the pattern to be produced. Subsequent developing of the resist removes either irradiated portions 108 or un-irradiated portions 110 to produce the desired pattern 112 on the substrate 104. The dimensions and the quality of the pattern depend on the optical system and the
20 properties of the resist. For example, in the lithography process when a laser beam is used, the critical size to be produced is dependent on the properties of the resist and a spot size of the laser beam. The reactivity of the resist is determined by the total irradiation amounts of the laser beam, i.e. the number of photons or electrons absorbed by the resist. As a result, the accumulation effect of the absorption in the resist affects
25 the precise definition of the shape and size of the generated pattern. Further, the spot size of the laser beam is determined by a laser wavelength λ and a numerical aperture (NA) of an objective lens used in the lithography system. A fine pattern can be formed by using a laser with a shorter wavelength and an objective lens with a higher NA.

30 Conventional lithography technologies, e.g. deep UV lithography and E-beam lithography, employ organic photosensitive materials as the resist to generate patterns through photo-induced chemical reaction between the resist and the laser beam or the electron beam. However, the generation of deep UV laser light usually requires a

complicated optical system, as disclosed in US Patent No. 2003/0133402 A1, to convert a long wavelength laser beam (e.g. about 1064 nm) to a short wavelength laser beam (e.g. about 266 nm). On the other hand, the E-beam system needs a large vacuum chamber that contains a high-precision mechanical system consisting mainly of an air-spindle motor and a translation stage. It is difficult to attain high accuracy and high-speed rotation of the spindle motor simultaneously in the high-vacuum chamber [Japanese Journal of Applied Physics, Vol. 40, pp. 1653 (2001)]. Therefore, the complicated systems of the deep UV lithography system and the E-beam lithography system are not commonly used due to inherent high production cost and rigid requirement of processing environment.

A phase change lithography technology, disclosed in US Patent No. 2005/0106508 A1, used a chalcogenide semiconductor phase change material as an inorganic resist, which was deposited on a Si substrate. A modulated laser beam was employed to generate amorphous patterns in the crystalline background from the side opposite to the substrate side. Before development of the chalcogenide phase change layer, the dielectric layer was etched away by means of reactive ion etching (RIE). The phase change layer was dipped in an alkaline solution to develop the patterns. The patterns were formed due to a difference in solubility of the phase change material in the amorphous and crystalline states. However, the media structure employed was complicated for optical disc mastery, which leads to a complicated development process.

WO 2006/045332 A1 discloses a mastering process using chalcogenide semiconductor phase change materials, which simplifies the media structure for mastery applications. US Patent No. 2005/0161842 A1 discloses WO_x and amorphous Si used as an alternative inorganic resist for mastery application. In addition, ZnS-SiO_2 and a chalcogenide semiconductor phase change material were proposed as an alternative resist for nanopatterning that could reduce the pattern size [Japanese Journal of Applied Physics, Vol. 45, pp. 1410 (2006)]. A three layers structure with a chalcogenide semiconductor phase-change material GeSbTe as an optical absorption layer was used. As the laser exposure is from the opposite side of the substrate, it can create tapered pattern which may be difficult to exfoliate during stamp fabrication for mastery application.

With the rapid development of miniature electronic, optical and micromechanical devices, sub micro-sized patterning becomes a necessary process step in the manufacturing process. Hence, there is a need to provide a method of generating a desired pattern on a substrate to address or overcome at least one of the above
5 problems.

SUMMARY

10 In accordance with a first aspect of the present invention there is provided a method of generating a pattern on a substrate, the method comprising forming a resist structure on the substrate, wherein the resist structure comprises at least a metallic glass thermal absorption layer, irradiating the resist structure with an energy beam, and developing the irradiated resist structure to form the pattern.

15 The resist structure may comprise an active layer deposited on the metallic glass thermal absorption layer.

The developing of the irradiated resist structure to form the pattern may comprise etching the active layer on the metallic glass thermal absorption layer.

20

The developing of the irradiated resist structure to form the pattern may further comprise etching the metallic glass thermal absorption layer after the etching of the active layer.

25 The resist structure may further comprise a dielectric layer desposited between the metallic glass thermal absorption layer and the substrate.

The developing of the irradiated resist structure to form the pattern may comprise etching the dielectric layer after etching the metallic glass thermal absorption layer.

30

The metallic glass thermal absorption layer may comprise one or more of a group consisting of Al-based, Mg-based, Pd-based, and Zr-based metallic glasses.

The metallic glass thermal absorption layer may comprise one or more metal elements of a group consisting of Al, Ni, Gd, Pd, Cu, Mg, Y, Zr, Ti, Pt, Ag, Pr, La, Hf, Ir, and mixtures or alloys.

5 The metallic glass thermal absorption layer has a thickness in the range of 5 nm to 50 nm.

The active layer may comprise one or more of a group consisting of oxide, nitride, fluoride, and carbide of a metal.

10

The active layer may comprise one of a group consisting of ZnS-SiO₂, AlN, Si₃N₄, ZrO₂-SiO₂.

The dielectric layer may comprise ZnS-SiO₂.

15

The substrate may comprise one or more of a group consisting of polycarbonate, polymethyl methacrylate, amorphous polyolefin, ceramic, quartz, silica and glass.

20

The energy beam may comprise one of a group consisting of a laser beam, an electron beam and an ion beam.

The method may further comprise discrete pattern formation by modulating a laser power in a form of pulse train over a range of rotation speeds of the substrate with different writing strategies in different rotation speed groups.

25

The method may comprise (a). a recording strategy for an intermediate rotation speed, (b) a recording strategy with a shorter pulse for a slow rotation speed, (c) a recording strategy with a castle shape waveform for a high rotation speed.

30

The resist structure may be prepared by one or more of a group consisting of vacuum deposition, electron beam vacuum deposition, chemical vapor deposition, ion plating, sputtering, and evaporation.

The developing of the irradiated resist structure to form the pattern may comprise a wet chemical etch process, adry etch process, or both.

5 In accordance with a second aspect of the present invention there is provided a pattern formed on a substrate using the method as defined in the first aspect.

BRIEF DESCRIPTION OF THE DRAWINGS

10

Embodiments of the invention will be better understood and readily apparent to one of ordinary skill in the art from the following written description, by way of example only, and in conjunction with the drawings, in which:

15 Figures 1A to 1C are schematic drawings illustrating a typical lithography process;

Figures 2A to 2C are schematic drawings illustrating a pattern generation process on a three layers resist structure according to an embodiment;

20

Figure 3A shows a graph of simulated temperature plotted against a distance along tracking direction according to the embodiment;

25 Figure 3B shows a graph of simulated temperature plotted against a distance along thickness direction according to the embodiment.

Figure 4 shows a laser pulse train used for the pattern generation process according to the embodiment;

30 Figures 5A and 5B show atomic force microscope (AFM) measurement results of the 3T pattern generated on the surface of the resist structure in 8x8 μm and 2x2 μm area respectively, according to the embodiment;

Figure 6A shows graphs of thickness of as-deposited ZnS-SiO₂ samples and annealed ZnS-SiO₂ samples plotted against etching time respectively according to the embodiment;

5 Figure 6B shows graphs of surface roughness of the as-deposited ZnS-SiO₂ samples and the annealed ZnS-SiO₂ samples plotted against etching time respectively, according to the embodiment;

10 Figures 7A and 7B show atomic force microscope (AFM) measurement results of a line pattern generated on the surface of the resist structure in 8x8 μm and 2x2 μm area respectively, according to another embodiment;

15 Figures 8A to 8E are schematic drawings illustrating a pattern generation process on a resist structure according to another embodiment;

Figure 9A shows a graph of etching rates of AlN and Si₃N₄ active layers plotted against annealing temperatures respectively according to another embodiment;

20 Figure 9B shows a graph of surface roughness of the AlN and Si₃N₄ active layers plotted against annealing temperatures respectively according to another embodiment;

Figure 10A shows a graph of etching rates of ZrO₂-SiO₂ samples plotted against respective annealing temperatures according to another embodiment;

25 Figure 10B shows a graph of surface roughness of the ZrO₂-SiO₂ samples plotted against respective annealing temperatures, according to another embodiment;

30 Figures 11(a) to 11(c) show writing strategies for pattern generation for intermediate speed, slow speed and high speed respectively, according to another embodiment;

Figures 12A to 12C are schematic drawings illustrating a pattern generation process on a two layers resist structure according to another embodiment;

Figure 13 shows a schematic diagram of an optical writing system for use in embodiments of the present invention.

Figure 14 shows a flowchart 1400 illustrating method of generating a desired pattern on a substrate according to an example embodiment.

DETAILED DESCRIPTION

Figure 2A shows a schematic drawing of a laser thermal lithography resist structure 200 in an example embodiment. The resist structure 200 comprises an approximately 0.6mm thick polycarbonate substrate 202 and a pattern generation layer which is referred to as inorganic resist layer 204. The inorganic resist layer 204 comprises an approximately 110 nm thick ZnS-SiO₂ lower dielectric layer 206, an approximately 20 nm thermal absorption AlNiGd metallic glass layer 208 and an approximately 100 nm thick ZnS-SiO₂ active layer 210. The lower dielectric layer 206 is deposited on the substrate 202 by radio frequency (RF) sputtering while the metallic glass layer 208 is deposited on the lower dielectric layer 206 by direct current (DC) magnetron sputtering. The background vacuum is about 1.2×10^{-7} mbar and the work pressure is about 4.5 to about 5.5×10^{-3} mbar with Ar as the processing gas at about 15 sccm flow rate.

The lower dielectric layer 206 is used to adjust an optical property of the medium and to protect the substrate 202. The refractive index of the lower dielectric layer 206 can be in the range of about 1.5 to about 5. The active layer 210 is used for pattern formation. The active layer 210 has a thermal conductivity of about 0.01 J/mKs to about 500 J/mKs. The thickness of the active layer 210 is dependent on the pattern requirements. The thickness of both the active layer 210 and lower dielectric layer 206 can be set within the range of about 5 nm to about 300 nm. The metallic glass layer 208 functions as a heat sink and a pattern generator, which absorbs the laser energy defining the pattern shape and size. The thickness of the metallic glass layer 208 can be in the range of about 5 to about 50 nm. The heat absorbed by the metallic glass layer 208 eventually transfers to both the active layer 210 and the lower dielectric layer 206, depending on the laser power and the writing strategy.

Heat distribution over a whole medium stack is a factor affecting pattern generation, which can be controlled by varying medium stack structure, laser power and writing strategy. Finite element method (FEM) is used to simulate temperature distribution of a thin film stack having the structure of the resist structure 200. Figure 3A shows a graph 300 of simulated temperature plotted against a distance along the tracking direction with a 3T laser pulse. The graph 300 shows simulation results of a temperature profile at an interface between a thermal absorption layer and an active layer. It can be seen that the temperature distribution forms a bell shape and the peak temperature at the interface is about 400°C. Figure 3B shows a graph 302 of simulated temperature plotted against a distance along thickness direction. The graph 302 shows a temperature profile of the active layer along the thickness direction forms a bell shape. The temperatures of the active layer are about 300 °C to about 390°C.

In the example embodiment, the energy beam irradiates the resist from either the substrate side or the side opposite to the substrate. The metallic glass layer works as a thermal sinker and absorbs the energy, the active layer is heated just like the above simulation. At a peak temperature area corresponding to the bell shape of the temperature distribution (compare Figure 3B), the temperature of the active layer in this area is enough to result in a difference on the etching rate due to the annealing, so the etching area is formed. The resulting patterns are sequentially relieved by a development process. The shape and size of the discrete or continuous patterns can be advantageously controlled finely by resist structure and writing strategy in example embodiments of the invention.

The substrate 202 of the resist structure 200 can be made of materials including but not limited to polycarbonate, polymethyl methacrylate (PMMA), amorphous polyolefin, quartz, silica, ceramic and glass. In this embodiment, the substrate 202 can be disk-shaped with a diameter of at least about 180 mm and a thickness from about 0.6 mm to about 1.2 mm. Other shapes and dimensions of the substrate 202 can be used in different embodiments. The metallic glass layer 208 of the resist structure 200 can be made of materials including but not limited to Al-based or Mg-based or Pd-based or Zr-based metallic glass. The metallic glass includes at least one metal element selected from a group of elements of Al, Ni, Gd, Pd, Cu, Mg, Y, Zr, Ti and mixtures or alloys, and may be partially or even completely replaced by elements of Pt, Ag, Pr, La,

Hf, Ir, etc. The active layer 210 can be made of materials including but not limited to oxide, nitride, fluoride or carbide of a metal or a mixture, such as ZnS-SiO₂, AlN, Si₃N₄, ZrO₂-SiO₂

5 A selective exposure process is carried out on an exposing apparatus. The exposing apparatus is a prototype optical platform in this embodiment. An energy beam such as a laser beam having a wavelength of about 650 nm is irradiated on the resist structure 200 from the substrate side through an objective lens with a numerical aperture of about 0.65. The laser beam can irradiate the resist structure 200 from the side
10 opposite to the substrate 202 in other embodiments. In other embodiments, an electron beam or an ion beam can be used in place of the laser beam. The refractive index of the polycarbonate substrate is about 1.61. A laser pulse train is used to control a laser power level such that the exposed and unexposed regions correspond to the pattern to be generated. The laser power was modulated to form the laser pulse train as shown in
15 Figure 4. The laser power can be controlled at three levels, i.e. the peak power P_w , the erase power P_e and the bottom power P_b . T is the reference clock duration, which is in the range of about 10 ns to about 100 ns. The leading laser pulse position is defined by the first pulse shift T_{fs} and the first pulse duration T_f . The consecutive pulse duration is defined by T_m , which is in the range of about 0.2T to about 0.9T. The last cooling pulse
20 duration is defined by T_{ls} . The peak power P_w , the erase power P_e and the bottom power P_b are chosen and optimized according to a rotation speed of the medium. In this embodiment, P_w is set at about 26 mW, P_e at about 1.4 mW and P_b at about 1.4 mW. After laser annealing, a chain of successive exposed regions 214 is formed in the as-deposited film by heating the metallic glass layer 208, as shown in Figure 2B.

25

 Figures 2A to 2C show the cross-section along the track direction of a disk in an example embodiment.

 A development process is then performed by immersing the exposed resist in a
30 chemical solution such as a hydrofluoride (HF) solution. In this embodiment, the HF solution is a diluted solution with a HF to water ratio of about 1:50. In other embodiments, the ratio can be set in the range of about 1:5 to about 1:500, depending on the pattern shape and size. The ratio is preferably set to be in the range of about 1:20 to about 1:100. A pattern 216 is formed in the active layer 210 as shown in Figure 2C.

Figures 5A and 5B show atomic force microscope (AFM) pictures of the generated 3T mark pattern at an about 8x8 μm scan and an about 2x2 μm scan respectively for an example embodiment. The height of the 3T pattern is about 60 nm and the length and the width are about 383 nm and about 313 nm respectively.

Figure 13 shows a schematic diagram of an optical writing system 1300 for use in embodiments of the present invention. The personal computer (PC) 1302 provides the graphical user interface for the user to control the optical writing system 1300. The PC 1302 also feeds data into the pulse generator 1304 for the generation of writing pulses via the driver 1306 and the laser diode (LD) 1308 to write on the resist on a disc 1310. The PC 1302 also communicates with the digital signal processor (DSP) 1312 to control other parts of the optical writing system. The servo system 1314 used for focusing and tracking in the optical pickup head 1316 is coupled to the DSP 1312. The servo system 1314 is also coupled to the slide motor 1318 and the spindle motor 1320 via respective digital to analogue (D/A) converters 1319, 1321 and respective drivers 1323 and 1325. The spindle motor 1320 and the slide motor 1318 provide the spinning and linear translation of the disc 1310 under the control of the servo system 1314. The LD 1308 emits the laser for writing and feedback through the optics 1322. The photo diode (PD) 1324 of the optical pickup head 1316 provides the optical to electrical feedback required for RF signal detection. The PD 1324 is coupled via a pre amplifier 1326 and an analogue to digital (A/D) converter 1328 to the DSP 1312.

Another factor affecting the pattern generation is the difference in dissolving rate of active layer materials in HF solution under heat treatment. In a confidential experiment, two sets of samples were used to determine the dissolving rate of the active layer material ZnS-SiO₂. The ZnS-SiO₂ layer with a thickness of about 100 nm was deposited on a silicon (Si) wafer. One set of samples were annealed in vacuum at a temperature of about 400°C for about 15 minutes while the other set was kept in the as-deposited state. These samples were then dipped in a HF solution for different time durations. AFM measurements were subsequently carried out to determine the thickness of the active layer 210 after etching. Figure 6A shows graphs of thickness of the as-deposited ZnS-SiO₂ samples and the annealed ZnS-SiO₂ samples plotted against etch time respectively. Graph 602 shows the thickness of the as-deposited ZnS-SiO₂ samples

plotted against etch time and graph 604 shows the thickness of the annealed ZnS-SiO₂ samples plotted against etch time. It can be observed from graphs 602 and 604 that the dissolving rate of ZnS-SiO₂ samples in the as-deposited state and in the annealed state are about 7.5 nm/s about 0.18 nm/s respectively. The ratio of the dissolving rate of ZnS-SiO₂ samples in the as-deposited state to the dissolving rate of ZnS-SiO₂ samples in the annealed state is about 40:1. A high ratio of the dissolving rates is preferred for precise control of pattern shape and size. The ratio of the dissolving rates can be in the range of about 5:1 to about 100:1 and is preferably in the range of about 20:1 to about 50:1.

Further, a smooth pattern surface after the developing process is preferred for pattern transfer and master preparation. A rough surface may introduce low frequency noise and may affect pattern quality. Figure 6B shows graphs of surface roughness of the as-deposited ZnS-SiO₂ samples and the annealed ZnS-SiO₂ samples plotted against time respectively. Graph 606 shows the surface roughness of the as-deposited ZnS-SiO₂ samples plotted against etch time and graph 608 shows the surface roughness of the annealed ZnS-SiO₂ samples plotted against etch time. It can be observed from graphs 606 and 608 that the surface roughness of the as-deposited samples increase faster than that of the annealed samples. The surface roughness of the annealed samples remained below 2.0 nm after 360 seconds.

It is recognised by the inventors that formation of metallic glasses quenched from the melt relies principally on the ability to suppress the nucleation of (metastable or equilibrium) crystalline phases. This is usually achieved by a fast quenching rate of the order of about 10⁵ to about 10⁶ K s⁻¹ though Al-, Mg-, Ln- (Ln5Lanthanide metal), Zr-, Pd-, Ti-, Fe-, Co- and Ni-based amorphous alloys have been synthesized successfully. metallic glass as a recordable optical media has been disclosed in WO 2006/036123 A1. However, metallic glass has not been used in producing lithography resist technology.

It is recognised by the inventors that some empirical rules such as the confusion principle do not apply to the glass forming ability (GFA) in Al-based metallic glasses. The glass-forming system may suggest alloying approaches towards metallic glass formation and may be necessary for successful devitrification strategies.

It is recognised by the inventors that the ductility (especially in compression) and the fracture strength of metallic glasses can be improved simultaneously by developing a nanocomposite structure of small nanocrystals (about 5–20 nm in diameter) of high density (about 0.10 m) embedded in an amorphous matrix. This has been observed in Pd-based, Al-based, Mg-based and Zr-based metallic glasses. A nanocomposite microstructure can be achieved by demelting vitrifying the glasses at appropriate temperatures. However, complicated crystallization processes (e.g. primary, polymorphic and eutectic crystallization) may occur, depending on composition and annealing conditions, which may be detrimental to the mechanical properties. An ideal devitrified microstructure requires a high density ($>10^{20} \text{ m}^{-3}$) of fcc-Al nanocrystals with an optimal volume fraction of about 20% for ternary Al–TM–RE (TM5 transition metals, RE5rare earth elements) glasses. Such a high nanocrystalline density requires a high driving force for nucleation and very sluggish growth kinetics of the fcc-Al phase, while at the same time suppressing nucleation of other crystalline (metastable or equilibrium) compound phases. The phase diagram data for the ternary Al–Ni–Gd system consists of a partial 800°C isotherm in the composition range of 0<Gd<33 at.%. Recent phase equilibria studies of a partial 500°C isotherm in the composition range of Al 70 at.% by the inventors show that the ternary compound phase richest in Al has a chemistry of Al Ni Gd. The other known ternary compound phases in the Al-rich region are Al₄ NiGd , Al₇ Ni₃ Gd₂ , Al₃Ni₂ Gd₁ , Al₂ NiGd and AlNiGd are accepted without alterations because they do not occur in the phase field of current interest.

Although the metallic glass has been proposed as an optical recording medium in the prior art, using the phase change effect from amorphous to crystalline state, the use of metallic glass as a resist has not been disclosed or recognized in the prior art. In the example embodiments of the present invention, the metallic glass is used as a thermal absorb layer in the resist. However, it is noted that the example embodiments do not use the known phase change effect of the metallic glass. The use of metallic glass as the thermal absorb layer in the example embodiments has a number of advantages, including providing a cost-effective approach, high performance such as high selectivity & high height to width ratio, loose environment requirement, reliable & stable compared with existing thermal absorb layer materials, such as GeSbTe, AgInSbTe.

In another embodiment, a prototype optical platform equipped with an approximately 650 nm laser and an objective lens of about 0.65 NA is used to conduct an exposing process on the surface of the laser thermal lithography resist structure 200 of Figure 2A. In the A continuous laser beam irradiates the resist from the polycarbonate substrate side 212 at a rotation speed of about 6.98 m/s. The laser beam can irradiate the resist structure 200 from the side opposite to the substrate 202 in other embodiments. In other embodiments, an electron beam or an ion beam can be used in place of the laser beam. The value of peak power is set at about 18 mW. The resist is dipped in a HF solution with a HF to water ratio of about 1:50. A continuous line pattern is generated on the surface of the metallic glass layer 208.

It is noted that the continuous laser in the prototype optical platform and the pulse train that can be used in the described example embodiments have a big difference. The continuous laser uses a constant power at any time in the writing process, while the pulse train has the variable laser power dependant on the pulse duration and pulse shift during the writing process as shown in Figure 4. The peak power for writing and the rotation speed of the substrate can be optimized and matched for the desired pattern. For completeness, it is also noted that because the substrate is rotating with the spindle motor in the writing system, the pattern line is a spiral line in the whole substrate surface. But in the micrometer range shown in the Figures, the line appears as a straight line.

AFM measurements are carried out for the developed medium. Figures 7A and 7b show drawings of the line pattern at an about 8x8 μm scan and an about 2x2 μm scan respectively in an example embodiment. The height of the line pattern is about 112 nm and the width of the line pattern is about 375 nm. The results also showed the height to width ratio of resist using AlNiGd (i.e. about 29.87%) is better than the resist using chalcogenide semiconductor material GeTe (i.e. about 21.95%) and Ge₂Sb₂Te₅ (i.e. about 21.40%). The height and width of the line pattern can be varied by varying the resist structure, rotation speed, laser power, writing strategy and development process. The height of the line pattern can be in the range of about 1 nm to about 2000 nm, and is preferably in the range of about 5 nm to about 500 nm. The width of the line pattern can be in the range of about 50 nm to about 5000 nm, and is preferably in the range of about 100 nm to about 2000 nm.

Figure 8A shows a schematic drawing of another laser thermal lithography resist structure 800. The resist structure 800 comprises an approximately 0.6mm thick polycarbonate substrate 802 and a pattern generation layer which is referred to as inorganic resist layer 804. The inorganic resist layer comprises an approximately 110 nm thick ZnS-SiO₂ lower dielectric layer 806, an approximately 20 nm thermal absorption AlNiGd metallic glass layer 810 and an approximately 100 nm thick ZnS-SiO₂ active layer 812. The lower dielectric layer 806 is deposited on the substrate 802 by RF sputtering while the metallic glass layer 808 is deposited on the lower dielectric layer 806 by DC magnetron sputtering. The background vacuum is about 1.2×10^{-7} mbar and the work pressure is about 4.5 to about 5.5×10^{-3} mbar with Ar as the processing gas at about 15 sccm flow rate.

Subsequently, a prototype optical platform equipped with a 650 nm laser and an objective lens of 0.65 NA is used to conduct an exposing process on the surface of the resist structure 800. A laser beam irradiates the resist structure 800 from the substrate side 812 in this embodiment. The laser beam can irradiate the resist 800 from the side opposite to the substrate 802 in other embodiments. In other embodiments, an electron beam or an ion beam can be used in place of the laser beam. Figure 8B shows a chain of successive exposed regions 814 formed in the metallic glass layer 808 by heating the metallic glass layer 808. The resist structure 800 is developed in a HF solution with a HF to water ratio of about 1:50. Figure 8C shows a pattern 816 formed on the surface of the metallic glass layer 808. The height and width of the pattern 816 can be varied by varying resist structure, rotation speed, laser power, writing strategy and development process.

The resist structure 800 can be further processed by immersing the resist structure 800 in another chemical solution, such as an alkaline solution. Figure 8D shows a pattern 818 being generated in the metallic glass layer 808. A new pattern 820 consisting of patterns 816 and 818 is formed. The thickness of the new pattern 820 is dependent on the thickness of the metallic glass layer 808 and the active layer 810. The new pattern 820 is formed on a top surface of the lower dielectric layer 806.

Since both the lower dielectric layer 806 and the active layer 810 are made of ZnS-SiO₂, the resist structure 800 can be further processed by immersing the resist structure 800 in the HF solution. Figure 8E shows a pattern 822 being generated in the lower dielectric layer 806, which is similar to the pattern 816 in the active layer 810. A new pattern 824 consisting of patterns 816, 818 and 822 is formed. The thickness of the new pattern 824 is dependent on the thickness of the lower dielectric layer 806, the metallic glass layer 808 and the active layer 810. The new pattern 824 is formed on a top surface of the substrate 802.

The patterns can be formed by selectively removing materials of each pattern generation layer. The depths of the various patterns can be varied by using a variety of developing solutions for the developing process. The height of the pattern can be in the range of about 1 nm to about 2000 nm, and is preferably in the range of about 5 nm to about 500 nm. The width of the pattern can be in the range of about 50 nm to about 5000 nm, and is preferably in the range of about 100 nm to about 2000 nm.

In another embodiment, nitride based dielectric materials such as AlN and Si₃N₄ are used for the active layer of the resists described above. One factor affecting the pattern generation is the difference in dissolving rate of the nitride based dielectric materials in HF solution under heat treatment. In a confidential experiment, 5 sets of samples were prepared to determine the dissolving rate of the nitride based dielectric material with respect to temperature. A nitride based dielectric layer with a thickness of about 100 nm was deposited on a Si wafer. The first to fourth sets of samples were annealed in nitrogen at a temperature of approximately 200°C, 400°C, 600°C, and 800°C for about 0 minutes respectively while the last set was kept in an as-deposited state. These samples were dipped in a HF solution with a HF to water ratio of about 1:50 for constant time duration.

AFM measurements were subsequently carried out to determine the thickness of the samples after etching. The etch rates for all the respective 5 samples of AlN and Si₃N₄ are calculated and plotted as a function of temperature, as shown in Figure 9A. From Figure 9A, it can be observed that the dissolving rate of as-deposited Si₃N₄ sample in HF solution is about 5.5 times higher than that of annealed Si₃N₄ sample at 800°C. In addition, the dissolving rate of as-deposited AlN sample is about 7.4 times higher than

that of the annealed AlN sample at 800°C. A high ratio of the dissolving rates is preferred for precise control of pattern shape and size. The ratio of the dissolving rates can be in the range of about 5:1 to about 100:1.

5 Figure 9B shows a graph of surface roughness of the AlN samples and the Si₃N₄ samples plotted against annealing temperatures respectively. The surface roughness of the as-deposited samples and the 800°C annealed samples were below 3.0 nm after developing. Smooth pattern surface after developing process is preferred for pattern transfer and master preparation. Rough surface may introduce low frequency noise and
10 may affect pattern quality. In order to operate in the preferable ratio of dissolving rate range of about 20:1 to about 100:1, selection of an etchant, e.g. by using Phosphoric acid H₃PO₄ instead of HF, can improve selectivity.

 In another embodiment, oxide based dielectric materials, e.g. ZrO₂-SiO₂, are
15 used for the active layer of the resists described above. One factor affecting the pattern generation is the difference in dissolving rate of the oxide based dielectric materials, e.g. ZrO₂-SiO₂, in HF solution under heat treatment. In a confidential experiment, 5 sets of samples were prepared to determine the dissolving rate of the ZrO₂-SiO₂ material with respect to temperature. A ZrO₂-SiO₂ layer with a thickness of about 100 nm was
20 deposited on a Si wafer. The first to fourth sets of samples were annealed in nitrogen at a temperature of approximately 200°C, 400°C, 600°C, and 800°C for 30 minutes respectively while the last set was kept in an as-deposited state. These samples were dipped in a HF solution with a HF to water ratio of about 1:50 for constant time duration.

25 AFM measurements were subsequently carried out to determine the thickness after etching. The etch rates for all the 5 samples are calculated and plotted as a function of temperature, as shown in Figure 10A. From Figure 10A, it can be observed that the dissolving rate of as-deposited ZrO₂-SiO₂ sample in the HF solution is about 8.7 times higher than that of the annealed state ZrO₂-SiO₂ sample at 600°C. A high ratio of
30 the dissolving rates is preferred for precise control of pattern shape and size. The ratio of the dissolving rates can be in the range of about 5:1 to about 100:1.

 Figure 10B shows a graph of surface roughness of the ZrO₂-SiO₂ samples plotted against annealing temperatures. The surface roughness of the as-deposited

sample and the 600°C annealed sample were below 2.0 nm after developing. Smooth pattern surface after developing process is preferred for pattern transfer and master preparation. Rough surface may introduce low frequency noise and may affect pattern quality. In order to operate in the preferable ratio of dissolving rate range of about 20:1 to about 100:1, selection of an etchant, e.g. by using Phosphoric acid H_3PO_4 instead of HF, can improve selectivity.

As discussed above, the pattern generation can be controlled by varying the resist structure and the developing process. The other factor affecting the pattern generation is the writing strategy, especially for the high-speed pattern generation process which determines the heat distribution in the resist. Therefore, development of a multi-speed compatible writing strategy is preferred for the laser thermal lithography resists described above in order to control the shape and size of the pattern and to facilitate forming of a discrete pattern. A continuous pattern can be formed with a constant laser power over a range of rotation speeds.

For intermediate speeds, conventional writing strategy can be used with appropriate adjustments of recording powers. Figure 11(a) shows a 5T pulse train for the intermediate speeds with $P_w > P_e \geq P_b$. The pulse durations of the leading pulse and the consecutive pulses are dependent on the recording speed. The last pulse is called cooling pulse, which is used for controlling the well-defined mark shape at the end of the recorded mark. The cooling pulse duration T_{is} can be adjusted according to the recording speed and recording powers.

For slow speeds, it is preferred that heat diffusion in the whole medium stack is controlled. Excessive heat diffusion may deteriorate the shape and size of the pattern. The pulse duration of writing power P_w is greatly reduced in order to control the mark shape, as shown in Figure 11(b). A cooling pulse with duration from about 0 to about $0.9T$ is added before the first writing pulse to avoid overheating.

For high speeds, the reference clock duration T becomes short. Consequently, it may pose a problem in achieving effective heating and cooling of the whole medium stack. Since cooling rate increases with increase in the rotation speed, it is possible that insufficient heating may occur. One approach to solve this problem is to increase the

writing power. However, the laser power is limited. Another approach is to adjust the pulse train shape by increasing the cooling power P_b , for example, using a castle shape waveform with $P_b \geq P_e$, as shown in Figure 11(c). Hence, the thermal absorption layer can maintain sufficient temperature after the laser beam is turned off.

5

Figure 12A shows a schematic drawing of another laser thermal lithography resist structure 1200. The resist structure 1200 comprises an approximately 0.6mm thick polycarbonate substrate 1202 and a pattern generation layer which is also known as inorganic resist layer 1204. The inorganic resist layer 1204 comprises an approximately
10 20 nm thermal absorption AlNiGd metallic glass layer 1206 and an approximately 100 nm thick ZnS-SiO₂ active layer 1208. The metallic glass layer 1206 is deposited on the substrate 1202 by DC magnetron sputtering while the active layer 1208 is deposited on the metallic glass layer 1206 by RF sputtering. The background vacuum is about 1.2×10^{-7} mbar and the work pressure is about 4.5 to about 5.5×10^{-3} mbar with Ar as the
15 processing gas at about 15 sccm flow rate.

The thickness of the active layer 1208 can be set within the range of about 5 nm to about 300 nm. The active layer 1208 is used for pattern formation and the thickness of the active layer 1208 is dependent on the pattern requirements. The metallic glass layer
20 1206 functions as a heat sink and a pattern generator, which absorbs the laser energy defining the pattern shape and size. The thickness of the metallic glass layer 1206 is in the range of about 5 nm to about 50 nm. The heat absorbed by the metallic glass layer 1206 eventually transfers to the active layer 1208, depending on the laser power and the writing strategy. Heat distribution over a whole medium stack is a factor affecting pattern
25 generation, which can be controlled by varying medium stack structure, laser power and writing strategy.

The substrate 1202 of the resist structure 1200 can be made of materials including but not limited to polycarbonate, polymethyl methacrylate (PMMA), amorphous
30 polyolefin, ceramic and glass. In this embodiment, the substrate 1202 can be disk-shaped with a diameter of at least about 180 mm and a thickness of about 0.6 mm to about 1.2 mm or thicker. Other shapes and dimensions of the substrate 1202 can be used in different embodiments. The metallic glass layer 1206 of the resist structure 1200 can be made of materials including but not limited to Al-based or Mg-based or Pd-based

or Zr-based metallic glass, which include at least one metal element and are mainly selected from the group of elements of Al, Ni, Gd, Pd, Cu, Mg, Y, Zr, Ti and mixtures or alloys, and may be partially or even completely replaced by elements of Pt, Ag, Pr, La, Hf, Ir, Ag, etc.

5

A selective exposure process was carried out on an exposing apparatus using the above writing platform. A laser beam having a wavelength of about 650 nm was irradiated on the resist from the substrate side 1210 through an objective lens with a numerical aperture of about 0.65. The laser beam can irradiate the resist from the side
10 opposite to the substrate in other embodiments. In other embodiments, an electron beam or an ion beam can be used in place of the laser beam. A laser pulse train is used to control laser power level such that the exposed and unexposed regions correspond to the pattern to be generated. After laser annealing, a chain of successive exposed regions 1212 is formed in an as-deposited film by heating the metallic glass layer 1208,
15 as shown in Figure 12B. Next, a development process was performed by immersing the exposed resist structure 1200 in a chemical solution, e.g. a HF solution. A pattern 1216 is formed on the metallic glass layer 1208 as shown in Figure 12C.

Figure 14 shows a flowchart 1400 illustrating method of generating a desired
20 pattern on a substrate according to an example embodiment. At step 1402, a resist structure is formed on the substrate, wherein the resist structure comprises at least a metallic glass thermal absorption layer. At step 1404, the resist structure is irradiated with an energy beam. At step 1406, the irradiated resist structure is developed to form the desired pattern.

25

The method of manufacturing the laser thermal lithography resist of the embodiments is advantageously cost effective, reliable and stable. The method advantageously provides high performance such as high selectivity and high height to width ratio and a high-speed pattern generation and development process. The method
30 can be advantageously used in small and compact systems and does not require a strict environment requirement. Further, the method can advantageously use simple resists.

It will be appreciated by a person skilled in the art that numerous variations and/or modifications may be made to the present invention as shown in the specific

embodiments without departing from the spirit or scope of the invention as broadly described. The present embodiments are, therefore, to be considered in all respects to be illustrative and not restrictive.

CLAIMS

1. A method of generating a pattern on a substrate, the method comprising:
forming a resist structure on the substrate,
5 irradiating the resist structure with an energy beam, and
developing the irradiated resist structure to form the pattern,
wherein the resist structure comprises at least a metallic glass thermal
absorption layer.
- 10 2. The method as claimed in claim 1, wherein the resist structure comprises an
active layer deposited on the metallic glass thermal absorption layer.
3. The method as claimed in claim 2, wherein the developing of the irradiated resist
structure to form the pattern comprises etching the active layer on the metallic glass
15 thermal absorption layer.
4. The method as claimed in claim 3, wherein the developing of the irradiated resist
structure to form the pattern further comprises etching the metallic glass thermal
absorption layer after the etching of the active layer.
- 20 5. The method as claimed in any one of the preceding claims, wherein the resist
structure further comprises a dielectric layer deposited between the metallic glass
thermal absorption layer and the substrate.
- 25 6. The method as claimed in claim 5, wherein the developing of the irradiated resist
structure to form the pattern comprises etching the dielectric layer after etching the
metallic glass thermal absorption layer.
7. The method as claimed in any one of the preceding claims, wherein the metallic
30 glass thermal absorption layer comprises one or more of a group consisting of Al-based,
Mg-based, Pd-based, and Zr-based metallic glasses.
8. The method as claimed in any one of the preceding claims, wherein the metallic
glass thermal absorption layer comprises one or more metal elements of a group

consisting of Al, Ni, Gd, Pd, Cu, Mg, Y, Zr, Ti, Pt, Ag, Pr, La, Hf, Ir, and mixtures or alloys.

9. The method as claimed in any one of the preceding claims, wherein the metallic glass
5 thermal absorption layer has a thickness in the range of 5 nm to 50 nm.

10. The method as claimed in claim 2, wherein the active layer comprises one or more of a group consisting of oxide, nitride, fluoride, and carbide of a metal.

10 11. The method as claimed in claim 2, wherein the active layer comprises one of a group consisting of ZnS-SiO₂, AlN, Si₃N₄, ZrO₂-SiO₂.

12. The method as claimed in claim 5, wherein the dielectric layer comprises ZnS-SiO₂.

15

13. The method as claimed in any one of the preceding claims, wherein the substrate comprises one or more of a group consisting of polycarbonate, polymethyl methacrylate, amorphous polyolefin, ceramic, quartz, silica and glass.

20 14. The method as claimed in any one of the preceding claims, wherein the energy beam comprises one of a group consisting of a laser beam, an electron beam and an ion beam.

25 15. The method as claimed in any one of the preceding claims, further comprising discrete pattern formation by modulating a laser power in a form of pulse train over a range of rotation speeds of the substrate with different writing strategies in different rotation speed groups.

30 16. The method as claimed in claim 15, comprising:
(a). a recording strategy for an intermediate rotation speed.
(b). a recording strategy with a shorter pulse for a slow rotation speed.
(c). a recording strategy with a castle shape waveform for a high rotation speed.

17. The method as claimed in any one of the preceding claims, wherein said resist structure is prepared by one or more of a group consisting of vacuum deposition, electron beam vacuum deposition, chemical vapor deposition, ion plating, sputtering,
5 and evaporation.

18. The method as claimed in any one of the preceding claims, wherein the developing of the irradiated resist structure to form the pattern comprises a wet chemical etch process, adry etch process, or both.

10

19. A pattern formed on a substrate using the method as claimed in any one of the preceding claims.