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(54) **SUB-WAVELENGTH LITHOGRAPHY VIA RABI OSCILLATIONS**

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(57) **ABSTRACT**

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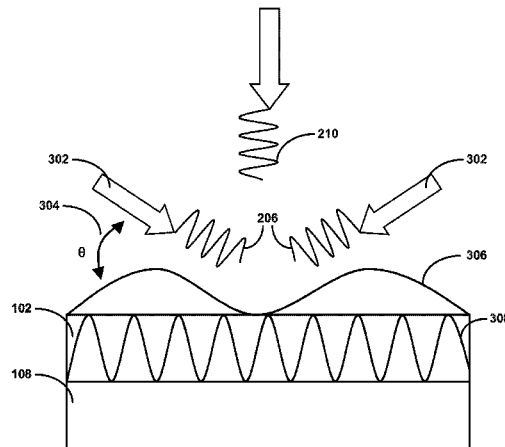
A sub-wavelength photolithographic method includes exposing a photoresist material to a stimulating electromagnetic source prior to further exposing the photoresist material to a dissociating electromagnetic source. The stimulating electromagnetic source induces Rabi oscillations in the photoresist material between a first molecular state and an excited molecular state. The subsequent exposure of the photoresist material to the dissociating electromagnetic source dissociates only those molecules that are in the excited state, altering the properties of the photoresist material in zones of excited state molecules. The resulting patterns therefore depend on the spatial distribution of the zones of excited state molecules induced by the stimulating electromagnetic source. The properties of the stimulating electromagnetic source are controlled to achieve a desired spatial distribution of zones of excited state molecules of the photoresist material.

Related U.S. Application Data

- (62) Division of application No. 13/270,597, filed on Oct. 11, 2011.
- (60) Provisional application No. 61/503,036, filed on Jun. 30, 2011.

- (51) **Int. Cl.**
G03F 7/20 (2006.01)
- (52) **U.S. Cl.**
USPC **430/322**
- (58) **Field of Classification Search**
USPC 430/322, 394
See application file for complete search history.

8 Claims, 10 Drawing Sheets



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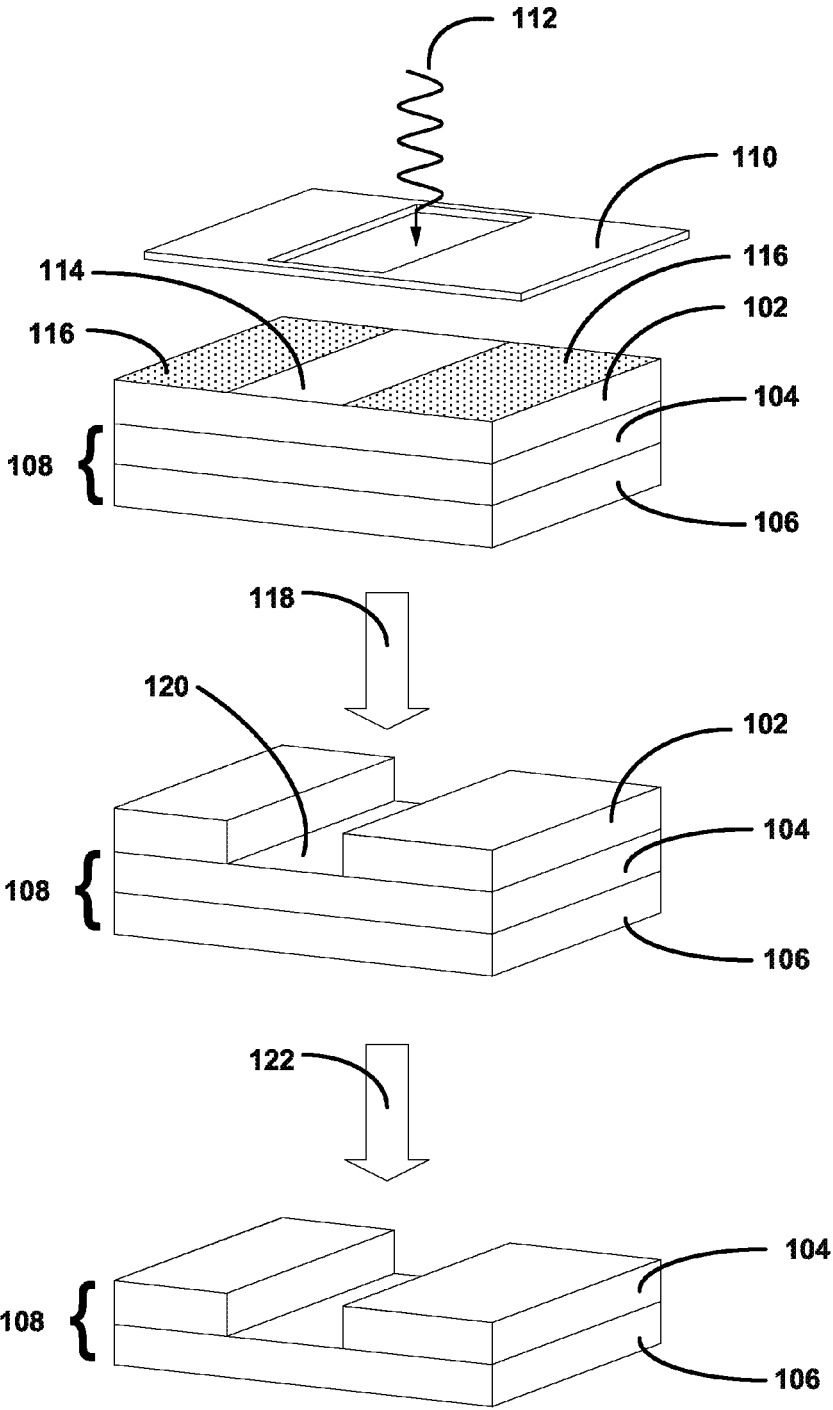


FIGURE 1

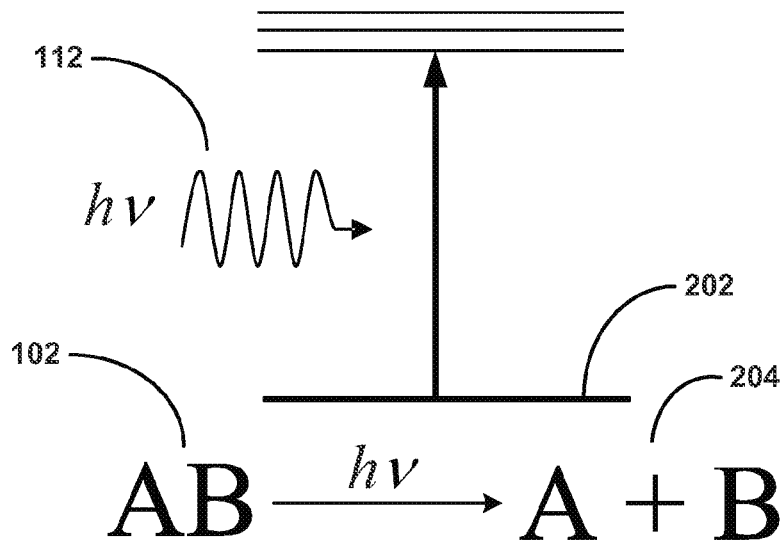


FIGURE 2A

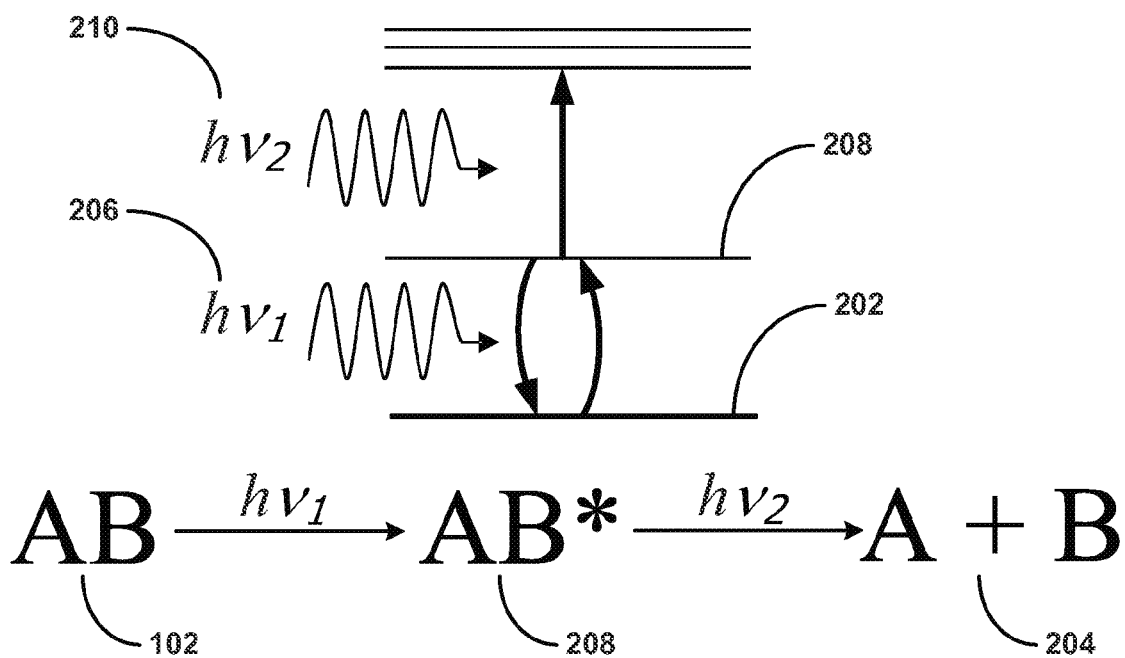


FIGURE 2B

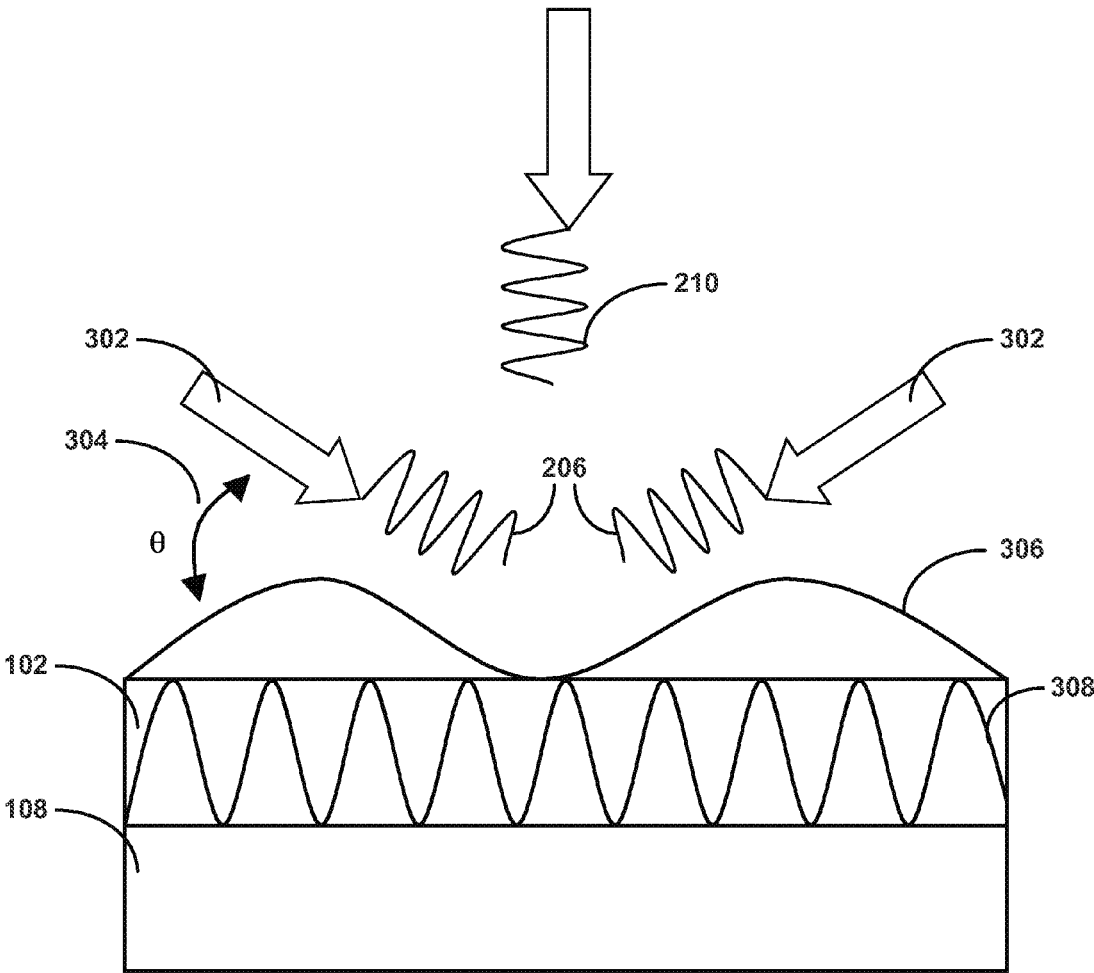


FIGURE 3

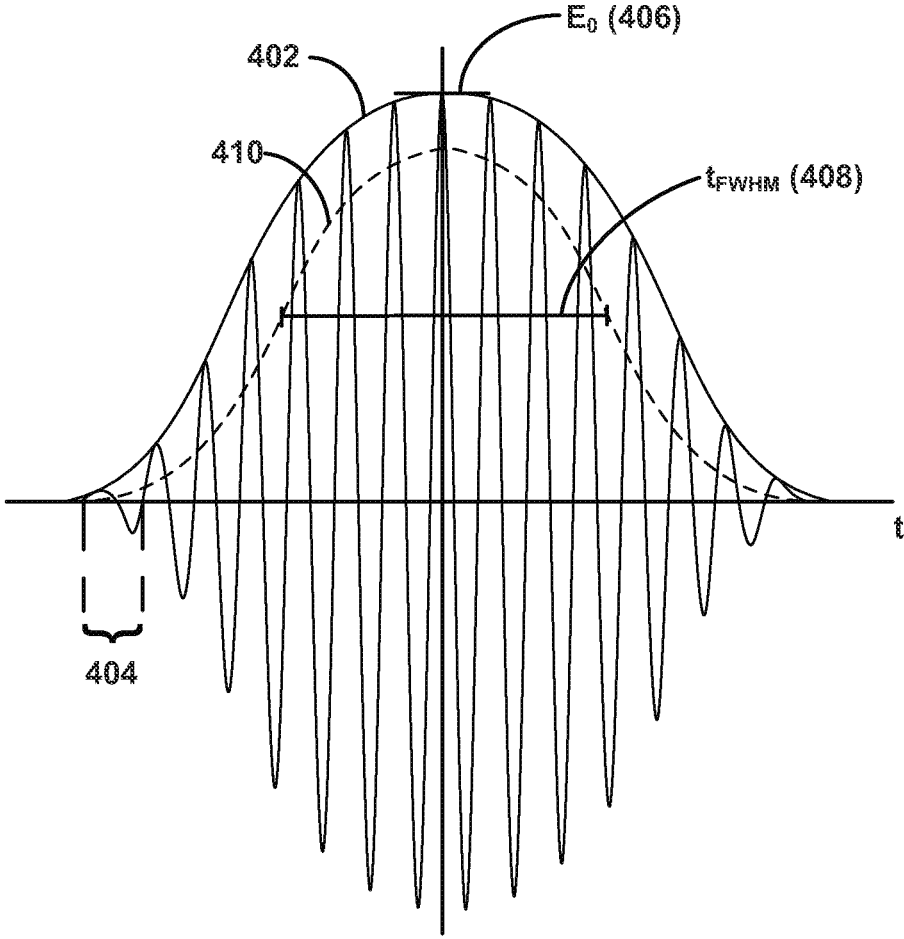


FIGURE 4

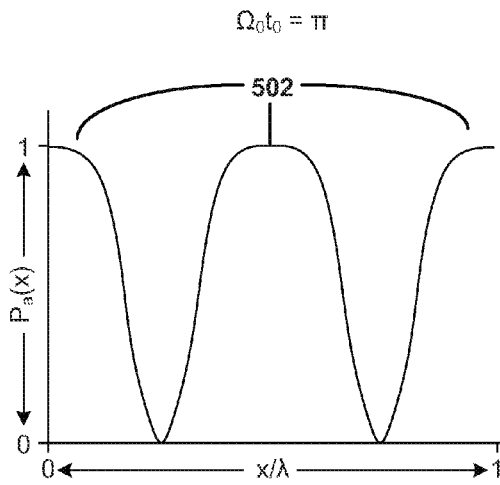


FIGURE 5A

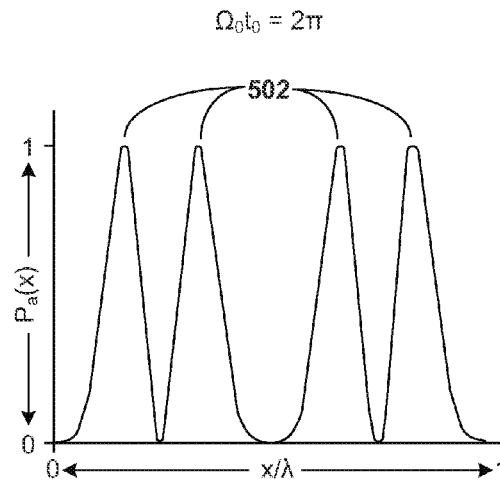


FIGURE 5B

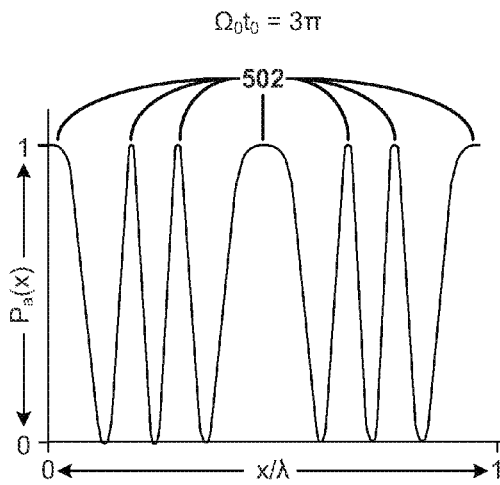


FIGURE 5C

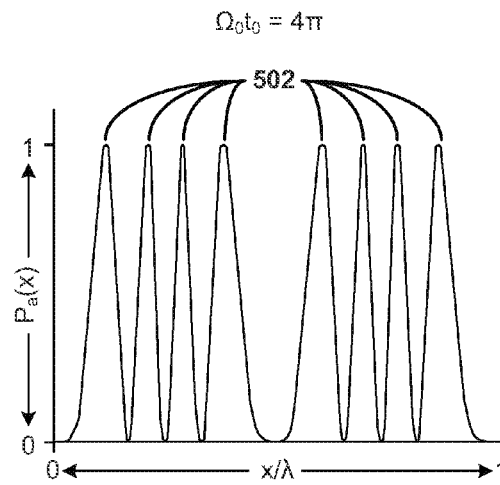


FIGURE 5D

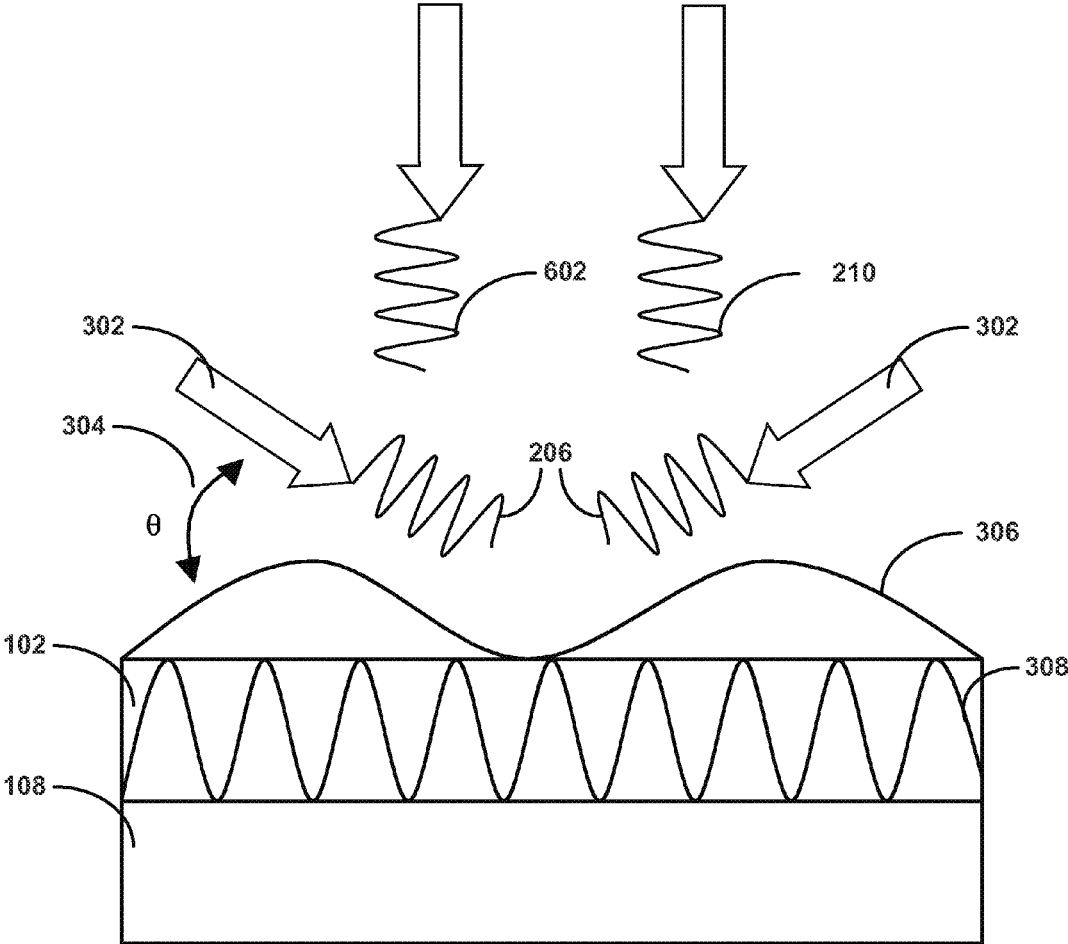


FIGURE 6

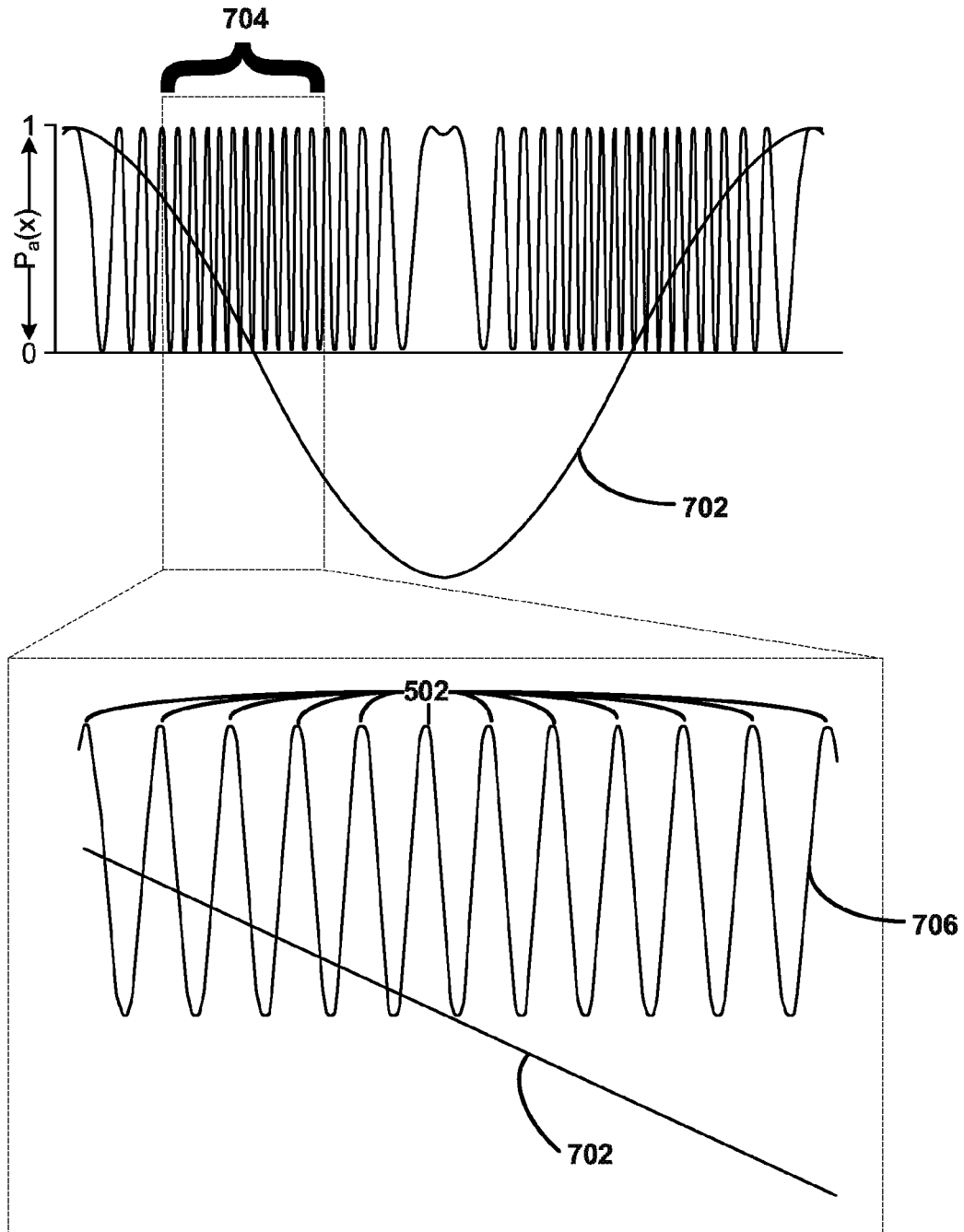


FIGURE 7

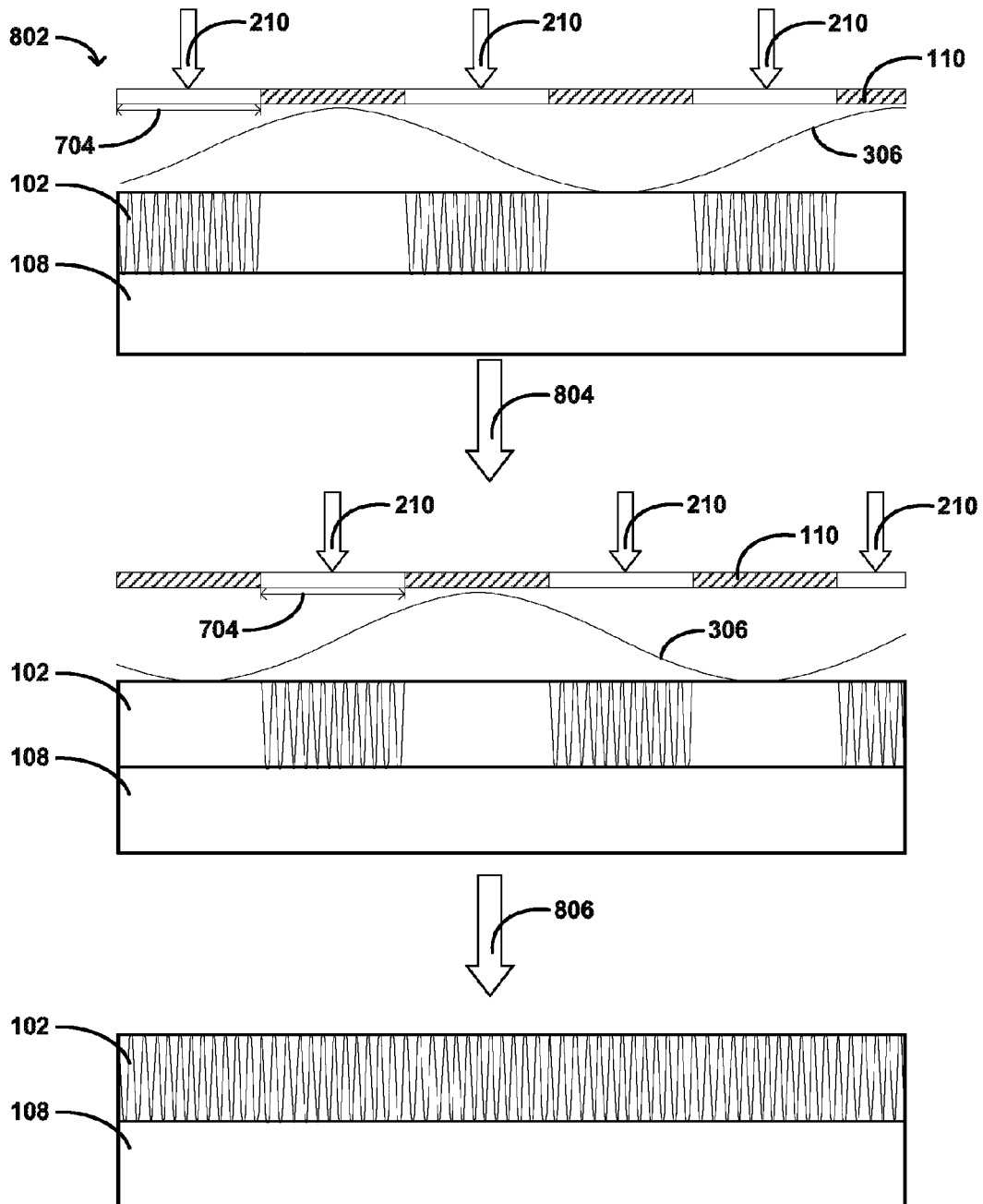


FIGURE 8

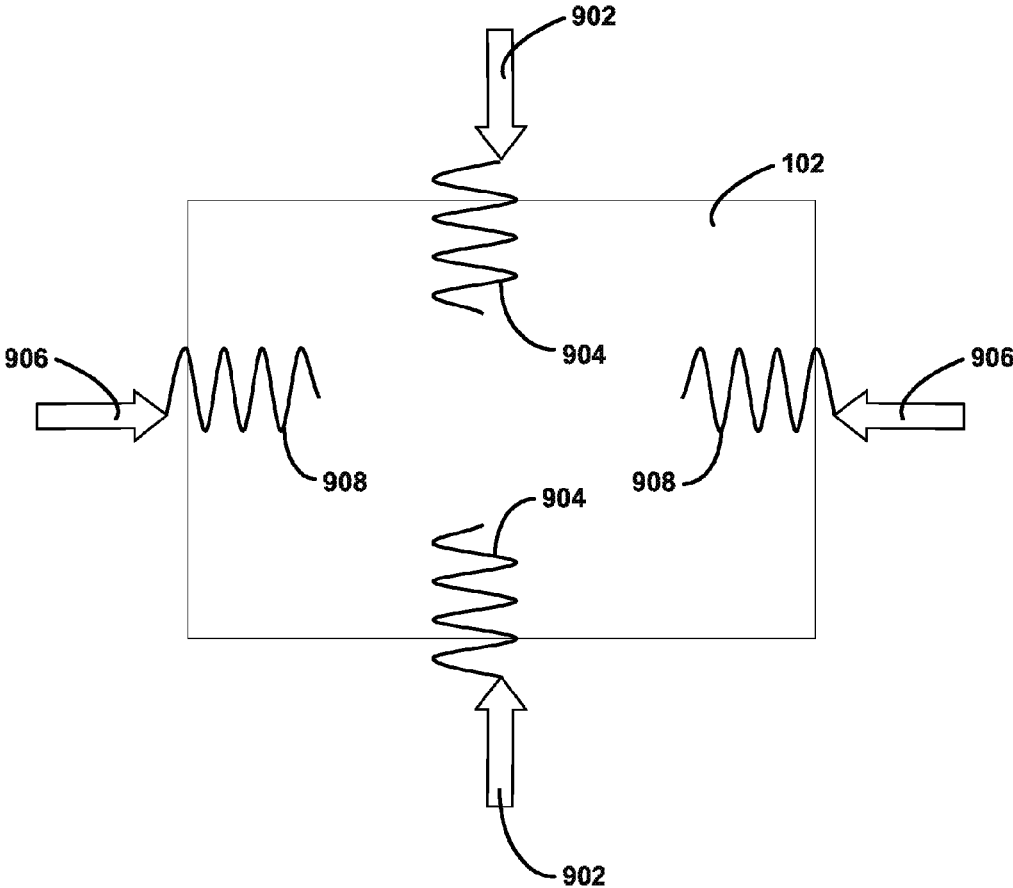


FIGURE 9

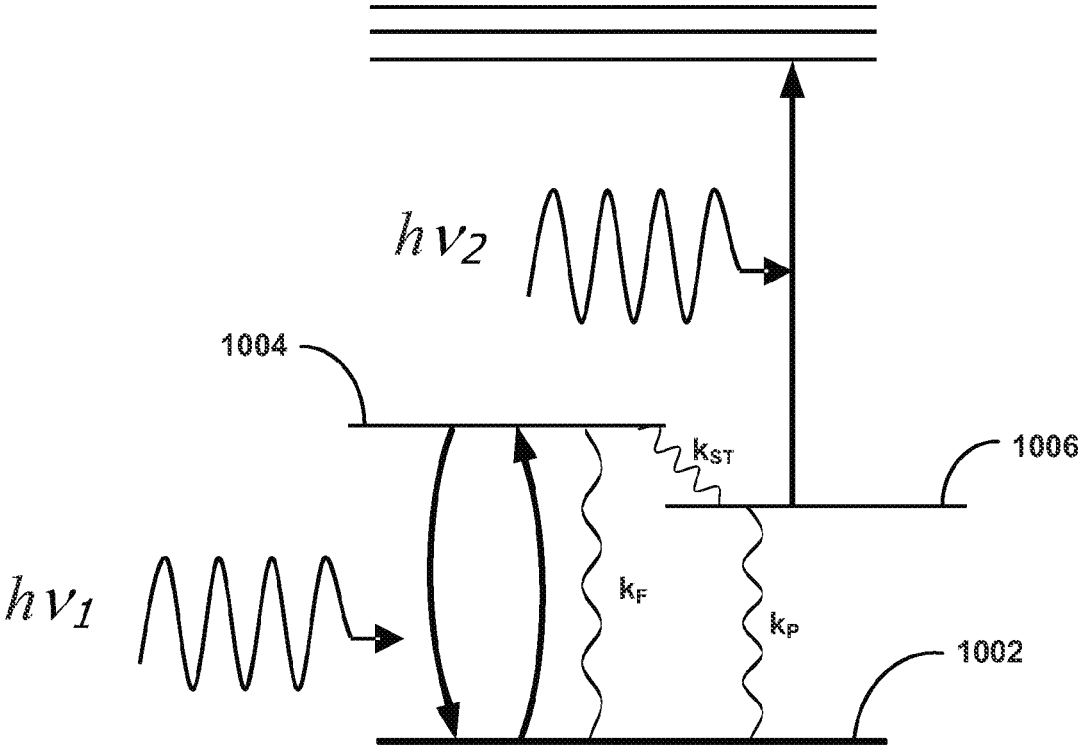


FIGURE 10

SUB-WAVELENGTH LITHOGRAPHY VIA RABI OSCILLATIONS

CROSS REFERENCE TO RELATED APPLICATIONS

This application is a divisional of U.S. application Ser. No. 13/270,597 entitled "Sub-wavelength Lithography via Rabi Oscillations" filed Oct. 11, 2011, which was in turn a non-provisional of U.S. Provisional Application Ser. No. 61/503,036 entitled "Sub-wavelength Lithography via Rabi Oscillations" filed Jun. 30, 2011. Priority is claimed to each of these applications, and each is incorporated herein by reference.

BACKGROUND

This disclosure relates generally to the field of photolithography. More particularly, but not by way of limitation, it relates to a sub-wavelength photolithographic technique that overcomes the diffraction limitations of traditional photolithography.

Photolithography is a critical step in the formation of the complex electronic circuitry that drives the modern devices (such as digital memory devices, video display devices, and digital imaging devices to name a few) to which we have become accustomed. The process of creating the semiconductor chips utilized by these modern devices typically involves several iterations of the photolithographic cycle.

Photolithography takes advantage of the altered properties of a light-sensitive substance known as a photoresist upon exposure to electromagnetic (EM) radiation. These altered properties of the photoresist material allow for the selective formation of various components of microelectronic circuits with features smaller than one micrometer. In a particular example of the traditional photolithographic process depicted in FIG. 1, for example, a photoresist **102** is applied to an insulating material **104** (such as silicon dioxide), which is itself disposed on a semiconductor material **106** (such as a silicon crystal), to form a substrate **108**. The photoresist **102** is typically applied by a spin coating process in which a liquid solution of the photoresist **102** is applied to the insulating material **104** while the substrate **108** is rapidly spinning. The spin coating process ensures that the photoresist **102** is applied in a uniform, flat layer.

A reticle **110** corresponding to a desired pattern is subsequently placed between an electromagnetic (EM) source **112** and the photoresist **102** such that certain portions of the photoresist **102** are exposed **114** upon activation of the EM source **112** while other portions of the photoresist **102** are unexposed **116**. While the particular example illustrated in FIG. 1 depicts a simple pattern for purposes of clarity, the photolithographic process can be utilized to create complex patterns with great precision.

As described above, the properties of exposed portion **114** of the photoresist **102** are altered based on exposure to EM source **112**. For example, exposed portion **114** of the photoresist **102** may be soluble in a particular solvent while unexposed portions **116** may be insoluble in the same solvent. Consequently, at step **118**, the exposed portion **114** of the photoresist **102** is selectively removed while the unexposed portions **116** of the photoresist **102** remain, creating an exposed portion **120** of insulating material **104**. It should be noted that the photoresist depicted in FIG. 1 is what is known as a positive photoresist, because the exposed portions of the photoresist become more soluble than the unexposed portions. Negative photoresists, in which the exposed portions of

the photoresist become less soluble than the unexposed portions, are also known and utilized.

At step **122**, the exposed portion **120** of insulating material **104** is removed (e.g., etched) by a known process while the portions of insulating material **104** that are protected by the remaining photoresist **102** are not removed. Subsequently, the remaining photoresist **102** is removed (e.g., dissolved in a solvent in which even the unexposed portions **116** of photoresist **102** are soluble), leaving the substrate **108** with the desired pattern. Subsequent photolithographic cycles may be utilized to further pattern the substrate **108** to form desired circuitry. While the process illustrated in FIG. 1 depicts the usage of photolithography to selectively remove material (in this case exposed portion **120** of insulating material **104**), the photolithographic process is equally applicable for the selective deposition of material. Thus, photolithography allows for the precise formation of microelectronic circuitry by the selective removal and deposition of materials on a substrate.

As the desire for smaller and more efficient electronic devices increases, there is a corresponding desire to form smaller patterns using photolithography to create the electrical circuitry that will drive these devices. It is well known, however, that diffraction limits the size of the features formed by traditional photolithography methods to approximately one half of the wavelength of the EM source **112** used to pattern the features according to the Rayleigh criterion. It would seem logical, therefore, to use an EM source **112** having a shorter wavelength. However, various problems arise with respect to shorter wavelength EM radiation. For example, as is well known, the wavelength of EM radiation is inversely proportional to the frequency of the EM radiation. Moreover, the frequency of EM radiation is directly proportional to the energy of the EM radiation. Thus, as wavelength decreases, frequency and energy increase. When insulating materials **104** such as silicon dioxide are exposed to photons with an energy greater than the band gap of the material, free electrons are released, thereby adversely affecting the insulating properties of the material. Furthermore, deep ultraviolet and x-ray radiation are significantly absorbed by traditional lenses and air such that they are not practical for usage in photolithography. There is thus a need to overcome the diffraction limit such that sub-wavelength patterns can be formed via photolithography.

Several attempts to achieve this goal have been proposed. A first interferometric approach requires entangled photon number states that are experimentally difficult to generate and sustain. A second approach, based on classical light pulses, achieves sub-wavelength resolution by correlating wave vector and frequency in a narrow band multi-photon detection process. This approach is based on an N-photon absorption process and can achieve a spatial resolution of $\lambda/(2N)$, where λ is the wavelength of the light. The multiphoton transition of this approach, however, is accompanied by the need for high light field intensities, which makes an experimental realization of the technique impractical. Finally, a method based on dark state physics that would achieve the same $\lambda/(2N)$ resolution without the N-photon absorption process has been proposed. This scheme relies on the preparation of the system in a position dependent trapping state via phase shifted standing wave patterns and employs resonant atom-field interactions only. The method, however, requires multibeam and multilambda systems, and is therefore also not practically realizable.

There is thus a need for a photolithographic method that overcomes the diffraction limit and is realizable using current technology such that sub-wavelength patterns can be formed via photolithography.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a perspective drawing illustrating the steps of a traditional photolithographic process.

FIG. 2A is a state diagram illustrating the transition of a photoresist according to a traditional photolithographic process.

FIG. 2B is a state diagram illustrating the transition of a photoresist according to an embodiment of the sub-wavelength photolithographic technique.

FIG. 3 is a block diagram of a photolithographic process according to an embodiment of the sub-wavelength photolithographic technique.

FIG. 4 is a graph illustrating properties of a stimulating pulse according to an embodiment of the sub-wavelength photolithographic technique.

FIGS. 5A-5D illustrate the locations of excited state molecules of a photoresist according to varying properties of a stimulating pulse according to an embodiment of the sub-wavelength photolithographic technique.

FIG. 6 is a block diagram of a photolithographic process according to an embodiment of the sub-wavelength photolithographic technique.

FIG. 7 is a graph illustrating the pattern of excited state molecules with respect to a particular stimulating pulse according to an embodiment of the sub-wavelength photolithographic technique.

FIG. 8 is a block diagram illustrating the isolation of periodic patterns of excited state molecules of a photoresist according to an embodiment of the sub-wavelength photolithographic technique.

FIG. 9 is a block diagram of a two-dimensional photolithographic process according to an embodiment of the sub-wavelength photolithographic technique.

FIG. 10 is a state diagram illustrating the quantum properties of a photoresist according to an embodiment of the sub-wavelength photolithographic technique.

DETAILED DESCRIPTION

Referring to FIGS. 2A and 2B, the general distinction between traditional photolithography and the sub-wavelength photolithographic technique of a particular embodiment of the invention is illustrated. FIG. 2A illustrates generally the transformation of a photoresist 102 in accordance with traditional photolithography as described above with respect to FIG. 1. Photoresist 102 (denoted as compound AB) is initially in a first state 202. Energy from EM source 112 initiates a reaction by which photoresist molecules 102 are excited from the first state 202 and react to form one or more reaction products 204 (denoted here as constituent A and constituent B) with different properties than that of photoresist 102. For example, constituent A and constituent B may both be soluble in a particular solvent while photoresist 102 (compound AB) is insoluble in the same solvent.

FIG. 2B, on the other hand, illustrates generally the transformation of a photoresist 102 in accordance with a particular embodiment of the sub-wavelength photolithographic technique disclosed herein. In the same manner as in the traditional technique described above with respect to FIG. 2A, photoresist 102 (compound AB) is initially in a first state 202. In the embodiment of the sub-wavelength photolithographic technique depicted in FIG. 2B, however, a first stimulating EM source 206 induces an oscillation between the first state 202 of the photoresist 102 and an excited state 208 (compound AB*) of the photoresist 102. In the presence of an oscillating field such as that created by first stimulating EM

source 206, an atom or molecule such as photoresist 102 can oscillate between a first state and an excited state by cyclically absorbing and emitting a quantum of energy. Oscillation between the first state 202 and the excited state 208 occurs by what are known in the art as Rabi oscillations. After the first stimulating EM source 206 induces oscillations between the first state 202 and the excited state 208, a dissociating EM source 210 initiates a reaction by which photoresist molecules 102 in the excited state 208 are dissociated and react to form reaction products 204 while photoresist molecules in the first state 202 do not react. The resulting patterns of the photoresist therefore depend on the spatial distribution of zones of photoresist molecules 102 in the excited state 208 induced by the first stimulating EM source 206 at the time the dissociating EM source 210 is activated. Therefore, the sub-wavelength photolithographic technique does not require a reticle 110 to form desired patterns but is instead based on the spatial distribution of zones of excited state 208 molecules. However, as will be described in further detail below, a reticle 110 may be utilized in an embodiment of the sub-wavelength technique to isolate zones of excited state 208 molecules in desired regions of the photoresist 102.

The description and illustration of the hypothetical chemical reactions in FIGS. 2A and 2B are not intended to be limiting in any manner. For example, neither the traditional nor the sub-wavelength photolithographic technique disclosed herein is limited to reactions in which a photoresist reacts to form its constituent parts. Instead, FIGS. 2A and 2B are intended to illustrate the difference between traditional photolithography and the sub-wavelength photolithographic technique of a particular embodiment of the invention.

Referring to FIG. 3, in an embodiment of the sub-wavelength photolithographic method of FIG. 2B, first stimulating EM source 206 is implemented as two beams 302 directed on the photoresist 102 from opposite directions forming an angle θ 304 with the horizontal. In one embodiment, the two beams 302 may be formed by two lasers. In another embodiment, a beam splitter may form the two beams 302 from a single source. While the two beams are described as directed onto the photoresist 102 from opposite directions, in alternate embodiments, the two beams 302 may be directed onto the photoresist according to a different spatial arrangement. The two beams 302 of first stimulating EM source 206 are implemented as Gaussian pulses having the same frequency ν_1 (the inverse of period 404), same maximal amplitude E_0 406, and same duration (full width at half maximum of intensity) $\tau_{FWHM} = 2\sqrt{\ln 2} \sigma$ 408 (where σ is the standard deviation of the Gaussian pulse) as illustrated by the amplitude profile 402 and intensity profile 410 of the Gaussian pulses in FIG. 4.

The two Gaussian pulses from beams 302 interfere with one another to form a standing electric field 306 described by:

$$E(x, t) = 2E_0 \exp\left(-\frac{t^2}{2\sigma^2}\right) \cos(kx \cos \theta + \phi) \cos(\nu_1 t)$$

where ϕ is the phase difference between the two pulses and ν_1 is resonant with the transition between the first state 202 and the excited state 208 of the photoresist 102. The frequency ν_1 of first stimulating EM source 206 will therefore vary depending on the photoresist material. For a typical photoresist material, the frequency of first stimulating EM source 206 might range from approximately 7.5×10^{14} Hz to 1.0×10^{15} Hz, corresponding to a wavelength in the range of 300 to 400 nanometers (nm). For example, poly(methyl methacrylate) (PMMA) is sensitive to wavelengths of approximately 300

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nm to 400 nm, diazonaphthoquinone (DNQ) is sensitive to wavelengths of approximately 300 nm to 450 nm, and epoxy-based photoresist SU-8 is sensitive to a wavelength of approximately 365 nm.

While first stimulating EM source **206** may correspond to the visible or UV portions of the EM spectrum for many common photoresist materials, the frequency of first stimulating EM source **206** is entirely based on the properties of the photoresist **102** and may correspond to any portion of the EM spectrum. For example, in one embodiment, the sub-wavelength photolithographic technique may be utilized to generate a nanopattern using a microwave field. If a first state **202** and excited state **208** of photoresist **102** correspond to an energy difference of approximately 3 GHz and the photoresist has a coherence time on the order of 1 second, a microwave pulse of wavelength 10 cm and duration 0.1 s would induce Rabi oscillations between the two states. If the associated Rabi frequency was approximately 0.1 GHz, a spatial resolution on the order of 10 nm could be obtained.

Because the frequency ν_1 is resonant with the transition between the first state **202** and the excited state **208** of photoresist **102**, the standing electric field **306** will induce a Rabi oscillation **308** between the first state **202** and the excited state **208** in photoresist **102**. The Rabi frequency corresponding to Rabi oscillation **308** generated by the standing electric field **306** is described by:

$$\Omega_R(x, t) = 2|\xi_{ba}|E_0 \exp\left(-\frac{t^2}{2\sigma^2}\right) \times \cos(kxc\cos\theta + \phi) / \hbar$$

where ξ_{ba} is the electric dipole moment between the first state **202** and the excited state **208** of photoresist **102** and \hbar is Planck's constant/ 2π .

Therefore, the frequency of the Rabi oscillation **308** induced by the first stimulating EM source **206** can be expressed as a function of position and time based on the properties of the photoresist **102** and the properties of the pulse of first stimulating EM source **206**. Moreover, according to the area theorem, the probability that a particular molecule of photoresist **102** at a particular position will be in the excited state **208** is given by:

$$P_a(x) = \frac{1 - \cos[\Omega_0 t_0 \cos(kxc\cos\theta + \phi)]}{2}$$

where

$$\Omega_0 = \frac{2|\xi_{ba}|E_0}{\hbar}$$

and

$$t_0 = \sqrt{\frac{\pi}{2} \ln 2} t_{FWHM}$$

the derivation of which is set forth in greater detail in U.S. Provisional Application Ser. No. 61/503,036, which is incorporated herein by reference. From the above equation, it is apparent that the excited state **208** molecules of photoresist **102** are located in a double cosine pattern which is dependent

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on the amplitude **406** and duration **408** of the Gaussian pulses of first stimulating EM source **206**.

For the simple case in which $\theta = \phi = 0$, where $\Omega_0 t_0 \ll 1$ (i.e., Gaussian pulses of first stimulating EM source **206** are weak and/or short), a linear approximation of the above equation specifying the location of the excited state **208** molecules shows that the spatial resolution that can be achieved via the sub-wavelength photolithographic method is similar to that of the diffraction limit of traditional photolithography (i.e., $\sim \lambda/2$). However, as is illustrated in FIGS. **5A** through **5D**, as the amplitude **406** and/or duration **408** of the Gaussian pulses are increased, the concentration of zones **502** of excited state **208** molecules of photoresist **102** per unit position is increased. For example, in FIG. **5A**, $\Omega_0 t_0 = \pi$, in FIG. **5B**, $\Omega_0 t_0 = 2\pi$, in FIG. **5C**, $\Omega_0 t_0 = 3\pi$, and in FIG. **5D**, $\Omega_0 t_0 = 4\pi$. While the positional scale in each of FIGS. **5A** through **5D** is constant (i.e., one wavelength), as the amplitude **406** and/or duration **408** of the Gaussian pulses are increased, there are more zones **502** of excited state **208** molecules per unit position.

As noted above with respect to FIG. **2B**, the subsequent exposure of photoresist **102** to dissociating EM source **210** will dissociate only those molecules of photoresist **102** in the excited state **208** to form reaction products **204** in zones **502** having altered properties from the unreacted photoresist **102**. Therefore, as the amplitude **406** and/or duration **408** of the Gaussian pulses are increased, there is a corresponding ability to pattern smaller features. Moreover, for a given set of variables corresponding to the Gaussian pulses of the first stimulating EM source **206**, the location of zones **502** of the excited state **208** molecules (and therefore the subsequently reacted portions of the photoresist **102**) can be determined. As used herein, zones **502** in which the photoresist **102** is in an excited state refer to positional regions of the photoresist **102** in which the likelihood that a particular photoresist molecule is in an excited state **208** is higher than in other positional regions of the photoresist **102**. Similarly, zones in which the photoresist **102** is in a first state refer to positional regions of the photoresist **102** in which the likelihood that a photoresist molecule is in a first state **202** is higher than in other positional regions of the photoresist **102**.

As is illustrated in FIGS. **5A** through **5D**, the excited state **208** molecules are not periodically distributed. There may therefore be a desire to identify and isolate regions of the photoresist **102** in which the location of zones **502** of excited state **208** molecules is periodic and to manipulate the spatial distribution and pattern of zones **502** of excited state **208** molecules within the isolated regions. In the embodiment illustrated in FIG. **6**, in addition to first stimulating EM source **206** directed on the photoresist **102** from opposite directions at an angle θ **304**, a background stimulating EM source **602** is directed on the photoresist **102** from a right angle. Again, in alternate embodiments, different spatial arrangements of first stimulating EM source **206** and background stimulating EM source **602** may be utilized. It is important to distinguish background stimulating EM source **602** from dissociating EM source **210**. Background stimulating EM source **602** is utilized in a similar manner as first stimulating EM source **206** to induce oscillations in the photoresist between first state **202** and excited state **208**. In one embodiment, background stimulating EM source **602** is implemented as a Gaussian pulse having the same frequency ν_1 **404** and duration t_{FWHM} **408** as the Gaussian pulses of the two beams **302** of first stimulating EM source **206**. Background stimulating EM source **602** may be activated simultaneously with first stimulating EM source **206** such that the two beams **302** of first stimulating EM source **206** interfere to form a standing wave and the back-

ground stimulating EM source 602 forms a constant background. In one embodiment, a beam splitter may be utilized to form both beams 302 of first stimulating EM source 206 as well as background stimulating EM source 602 from a single laser beam or other EM source. As will be described in greater detail below, the amplitude E_1 of the Gaussian pulse of background stimulating EM source 602 may be manipulated to control the pattern of the zones 502 of excited state 208 molecules of photoresist 102.

The resulting electric field created by the Gaussian pulses of the two beams 302 of first stimulating EM source 206 and the Gaussian pulse of background stimulating EM source 602 is given by:

$$E(x, t) \cong [2E_0 k x \cos \theta + E_1] \exp\left(-\frac{t^2}{2\sigma^2}\right) \cos(\nu_1 t)$$

when

$$\phi = \frac{\pi}{2}$$

and $n\pi - \epsilon \leq kx \cos \theta \leq n\pi + \epsilon$, where n is an integer and ϵ is a small number.

The intensity gradient of the electric field 702 produced by this arrangement is approximately constant over a region 704 as illustrated in FIG. 7. The location of zones 502 of excited state 208 molecules of photoresist 102 corresponding to electric field 702 is shown at 706. As further illustrated in FIG. 7, zones 502 of excited state molecules 208 of photoresist 102 are periodically distributed within region 704. The pattern 706 of excited state 208 molecules within region 704 is given by:

$$P_a(x) = \frac{1 - \cos(Ax + B)}{2}$$

where $A = \Omega_0 t_0 k \cos \theta$, $B = \Omega_1 t_0$, and $\Omega_1 = |\xi_{ab} E_1| / \hbar$. Thus, coefficients A and B can be controlled by the amplitudes of the Gaussian pulses of first stimulating EM source 206 and background stimulating EM source 602 (E_0 and E_1 , respectively) as well as the duration of the Gaussian pulses to achieve a desired periodic pattern within the region 704. For example, setting $B=0$ results in the location of excited state 208 molecules in the region 704 forming a cosine pattern while setting $B=\pi/2$ results in the location of excited state 208 molecules in the region 704 forming a sine pattern.

Region 704 is defined by

$$\frac{n\pi - \epsilon}{k \cos \theta} \leq x \leq \frac{n\pi + \epsilon}{k \cos \theta}$$

Accordingly, the region 704 over which a periodic pattern of zones 502 of excited state 208 molecules can be obtained is limited by the value of θ . Just by way of example, to generate a periodic pattern in a region 704 equivalent to 10λ , with $n=0$ and $\epsilon=\pi/4$, $\cos \theta=1/40$. Moreover, the spatial resolution of the zones 502 of excited state 208 molecules based on the periodic pattern obtained in region 704 is defined by $\lambda_{eff} = \lambda / \Omega_0 t_0 \cos \theta$ where λ_{eff} is the spatial resolution within region 704.

Thus, based on the above example in which $\cos \theta=1/40$, to obtain a resolution of $\lambda/10$ in region 704, $\Omega_0 t_0$ would be equal to 400.

As the size of region 704 increases, larger amplitude Gaussian pulses from the two beams 302 of first stimulating EM source 206 are required to obtain the same spatial resolution of the zones 502 of excited state 208 molecules within the region 704. At some point, the power requirements to obtain such a result over a larger region 704 might become very large and impractical. As depicted in FIG. 8, however, a particular embodiment of the sub-wavelength photolithographic technique utilizes the ability to shift the phase of the electric field 306 resulting from the Gaussian pulses of first stimulating EM source 206 and background stimulating EM source 602 in conjunction with a reticle 110 to isolate the portions of the photoresist 102 that are exposed to dissociating source 210 to those portions of the photoresist 102 in which the gradient of intensity of the electric field is constant. In these isolated regions, the spatial distribution of the zones 502 of excited state 208 molecules is periodic. In a first step 802, an electric field 306 is generated in the manner described above with respect to FIGS. 3 and 6. The system variables (such as pulse amplitude and pulse duration) are selected such that the gradient of intensity of electric field 306 is approximately constant in desired regions 704, thereby inducing a periodic pattern of zones 502 of excited state 208 molecules of photoresist 102 having the desired spatial resolution within regions 704. Subsequently, dissociating EM source 210 is activated. A reticle 110 exposes only those portions of photoresist 102 corresponding to regions 704 to dissociating EM source 210 and shields the portions of the photoresist not corresponding to regions 704 (in which the distribution of zones 502 of excited state 208 molecules is not periodic) from dissociating EM source 210. As has been described, dissociating EM source 210 is of an energy such that only those molecules of photoresist 102 that are in the excited state 208 at the time of exposure to dissociating EM source 210 dissociate to form reaction products 204. Thus, within the exposed regions of photoresist 102 corresponding to regions 704, a periodic pattern having a sub-wavelength spatial resolution is created.

Thereafter, at step 804, the properties of the Gaussian pulses used to generate electric field 306 are altered such that the phase of the electric field 306 is shifted. As demonstrated by a comparison of the electric field 306 generated in steps 802 and 804, the new regions 704 of electric field 306 over which the gradient of intensity is approximately constant is shifted in step 804 to correspond to the portions of the photoresist 102 that were not exposed to dissociating EM source 210 in step 802. Reticle 110 is also altered to correspond to new regions 704 such that new regions 704 are exposed to dissociating EM source 210. Dissociating EM source 210 is then activated to form the sub-wavelength pattern in the portions of photoresist 102 that were not exposed in step 802. Therefore, as illustrated in step 806, a desired periodic sub-wavelength pattern can be formed over a large region of photoresist 102 with the same power requirements as required to form the same pattern over a smaller region by exposing only the regions in which the pattern of excited state 208 molecules is periodic to dissociating EM source 210 and repeating the process after shifting the regions.

Each of the above embodiments has described one-dimensional applications. As will be described below, the disclosed photolithographic technique can be expanded to a two-dimensional application. Moreover, it should be noted that the described one-dimensional applications can be repeated sequentially to form two-dimensional patterns on a substrate.

For example, the one-dimensional patterns could be formed on a substrate and the substrate could be subsequently shifted before repeating the process to form desired two-dimensional patterns on the substrate.

Referring to FIG. 9, a top side view of a portion of a photoresist **102** illustrates an embodiment of the photolithographic technique that generates two-dimensional patterns. Just as described above with respect to FIGS. 3 and 6, beams are directed on the photoresist from an angle θ (not shown) with the surface of the photoresist **102**. However, in the depicted two-dimensional embodiment, there is a first pair of opposing beams **902** of first stimulating EM source **904** and a second pair of opposing beams **906** of second stimulating EM source **908**. The opposing beams **902** and **906** are depicted as perpendicular to each other, however, other spatial arrangements may also be utilized. Just as described above, the opposing beams **902** and **906** may be implemented as Gaussian pulses. The Rabi oscillations induced in the photoresist **102** by the opposing beams **902** and **906** will form zones of excited state **208** molecules over a two-dimensional area. As further described above, a background stimulating EM source (not shown) directed on the photoresist **102** may be implemented as a Gaussian pulse to provide a constant background electric field over the two-dimensional area. Furthermore, a dissociating EM source (not shown) may be activated to dissociate the excited state **208** molecules of photoresist **102** to form a desired pattern over the two-dimensional area.

The location of excited state **208** molecules over a two-dimensional region $\lambda \times \lambda$ can be simulated by the truncated Fourier series:

$$f(x, y) \approx \sum_{m=0}^M \sum_{n=0}^N \left\{ a_{mn} \cos \left[\frac{\sqrt{m^2 + n^2}}{\cos(\theta)} \cos \left[\frac{2\pi \cos(\theta)}{\lambda} \frac{(mx + ny)}{\sqrt{m^2 + n^2}} + \frac{\pi}{2} \right] \right] + \right. \\ b_{mn} \cos \left[\frac{\sqrt{m^2 + n^2}}{\cos(\theta)} \cos \left[\frac{2\pi \cos(\theta)}{\lambda} \frac{(mx - ny)}{\sqrt{m^2 + n^2}} + \frac{\pi}{2} \right] \right] + \\ c_{mn} \sin \left[\frac{\sqrt{m^2 + n^2}}{\cos(\theta)} \cos \left[\frac{2\pi \cos(\theta)}{\lambda} \frac{(mx + ny)}{\sqrt{m^2 + n^2}} + \frac{\pi}{2} \right] \right] + \\ \left. d_{mn} \sin \left[\frac{\sqrt{m^2 + n^2}}{\cos(\theta)} \cos \left[\frac{2\pi \cos(\theta)}{\lambda} \frac{(mx - ny)}{\sqrt{m^2 + n^2}} + \frac{\pi}{2} \right] \right] \right\}. \quad (35)$$

Therefore, the location of excited state **208** molecules in the two-dimensional area can be approximated by a Fourier series having four components. In the described embodiment, for the first and third components, the pulses are directed from directions $(m\hat{x} + n\hat{y})/\sqrt{m^2 + n^2}$, and for the second and fourth components, the pulses are directed from directions $(m\hat{x} - n\hat{y})/\sqrt{m^2 + n^2}$, with $\Omega_0 t_0 = \sqrt{m^2 + n^2}/\cos(\theta)$. Based on this approximation of the location of excited state **208** molecules over the two-dimensional area, it is possible to pattern arbitrary features such as alphanumeric characters using a sequence of pulses. For example, if $M=N=15$, there are $15 \times 15 \times 4$ Fourier components. For each component, there are four pulses (stimulating pulses from beams **902** and **906**, background stimulating pulse, and dissociating pulse). Thus, with $M=N=15$, an arbitrary pattern can be printed in a $\lambda \times \lambda$ two-dimensional region with 3600 pulses. Obviously, the resolution of the desired pattern can be increased with increased values of M and N or decreased with decreased values of M and N .

It is important to note that the quantum properties of photoresist **102** play an important role in the sub-wavelength

photolithographic method disclosed herein. FIG. 10 depicts a state energy diagram for a typical photoresist. States **1002** and **1004** represent the ground singlet state and the first excited singlet state, respectively. State **1006** represents the first excited triplet state. Because the transition between the singlet state and the triplet state is dipole forbidden, the state diagram is essentially equivalent to the two-level system described with respect to FIG. 2B. K_F represents the fluorescence decay rate from state **1004** to **1002**, K_P represents the phosphorescence decay rate from state **1006** to **1002**, and K_{ST} represents the intersystem crossing rate from state **1004** to **1006**. To induce Rabi oscillations, the system should stay coherent (i.e., in an excited quantum state). A typical decoherence time τ is approximately 1-5 picoseconds (ps) at room temperature due to interactions between neighboring molecules. To realize the disclosed sub-wavelength photolithographic technique, the requirements for these parameters are $t_0 \sim \tau$ and $K_{ST} \gg K_F \gg K_P$. Given these parameters, the lifetime of state **1006** (or phosphorescence time) is long. Within the phosphorescence time, dissociating EM source **210** is activated to dissociate the molecules in state **1006**. By way of example, for 1-bromonaphthalene, $K_F \sim 10^6$ Hz, $K_{ST} \sim 10^9$ Hz, and $K_P \sim 30$ Hz. Based on the equations set forth above, to generate a pattern with a spatial resolution of $\lambda/10$ over a region of 10λ , it would be sufficient to choose $t_0 = 5$ ps and $\Omega_0 \sim 8 \times 10^{13}$ Hz. The corresponding peak power, E_0 , would be 2.17 GW/cm². The lifetime of state **1006** for 1-bromonaphthalene is approximately 30 milliseconds (ms), which provides a sufficient amount of time to activate dissociating EM source **210**.

It should further be noted that the decoherence time, τ , of the photoresist **102** is an important factor in the sub-wavelength photolithographic technique. While the spatial resolution of the excited state **208** molecules is not affected by the decoherence time for a given set of system variables, visibility is decreased with decreasing decoherence time (i.e., the spatial distribution of zones of excited state **208** molecules is the same but the likelihood that a given molecule in such a zone is actually in excited state **208** is less than that in which decoherence time is ignored). As decoherence time decreases, a shorter stimulating EM source pulse of greater power is required to achieve the same spatial resolution and visibility.

It is to be understood that the above description is intended to be illustrative, and not restrictive. For example, the above-described embodiments may be used in combination with each other. Many other embodiments will be apparent to those of skill in the art upon reviewing the above description. The scope of the invention therefore should be determined with reference to the appended claims, along with the full scope of equivalents to which such claims are entitled.

What is claimed is:

1. A photolithographic method, comprising:

exposing a photoresist material to a stimulating electromagnetic source, the stimulating electromagnetic source stimulating a plurality of zones of the photoresist material into an excited state, wherein the zones are periodic in a first plurality of regions of the photoresist and are non-periodic in a second plurality of regions of the photoresist; and

exposing only the first plurality of regions to a dissociating electromagnetic source to obtain a periodic pattern of reacted photoresist material.

2. The photolithographic method of claim 1, wherein the stimulating electromagnetic source is implemented as two or more Gaussian pulses.

3. The photolithographic method of claim 2, wherein the Gaussian pulses have the same amplitude and duration.

4. The photolithographic method of claim 1, wherein a frequency of the stimulating electromagnetic source is resonant with an energy difference between a first state of the photoresist material and the excited state of the photoresist material. 5

5. The photolithographic method of claim 1, wherein the photoresist material is exposed to the dissociating electromagnetic source within a phosphorescence time of the photoresist material. 10

6. The photolithographic method of claim 1, wherein the stimulating electromagnetic source is implemented as two or more laser pulses.

7. The photolithographic method of claim 1, wherein the second plurality of regions of the photoresist material are shielded from exposure to the dissociating electromagnetic source by a reticle. 15

8. The photolithographic method of claim 1, further comprising: 20

after exposing the first plurality of regions to the dissociating electromagnetic source, exposing the photoresist material to a second stimulating electromagnetic source, the second stimulating electromagnetic source stimulating a plurality of zones of the photoresist material into an excited state, wherein the zones are periodic in the second plurality of regions of the photoresist and are non-periodic in the first plurality of regions of the photoresist; and 25

exposing only the second plurality of regions to the dissociating electromagnetic source to obtain the periodic pattern of reacted photoresist material. 30

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