Optical projection lithography at half the Rayleigh resolution limit by two-photon exposure

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Abstract. Photographic media can be exposed by two-photon absorption, rather than the more usual one-photon absorption. This leads to the question of whether the simultaneous absorption of a pair of photons could be accompanied by a twofold spatial-resolution enhancement. We find that ordinary two-photon absorption merely enhances the photographic contrast, or gamma. While this improves the spatial resolution somewhat, it does so at the expense of requiring tighter control over the incident light intensity. Instead, we introduce a new type of exposure arrangement employing a multiplicity of two-photon excitation frequencies, which interfere with one another to produce a stationary image that exhibits a true doubling of the spatial resolution. [S0091-3286(99)00402-X]

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The simultaneous absorption of a pair of photons has been studied experimentally[1] since high-power lasers became available in the 1960s. Two-photon absorption can occur in all media, with or without inversion symmetry. It is derived from a third-order susceptibility, and is distinct from second-harmonic generation, which originates from a second-order susceptibility.[2]

Since the total absorption is proportional to the square of the optical intensity, the peak optical power is very important. The recent developments in 10^{-13}-s laser pulse technology have made two-photon absorption into a more practical tool. For a long time, it has been possible to attain peak intensities $\approx 10^{13}$ W/cm^2, but now this can be done at a fluence of less than 1 J/cm^2, safely below the damage threshold of many transparent materials. Thereby we can have a high probability of two-photon exposure in photoresist, without burning or damaging the photopolymer.

Thus, in recent years, two-photon absorption has commenced to be used for exposing[3,4] photoresists. (The square-law intensity dependence restricts the exposure to the focal plane only. Multiple exposures allow the creation of three-dimensional structures.) It is natural to ask, then, what is the spatial resolution of two-photon lithography. There has already been some discussion of resolution limits in two-photon, scanning[5,6] confocal fluorescence microscopy. We will find that ordinary two-photon exposure of photoresist merely enhances the photographic contrast, or gamma. While this improves the spatial resolution somewhat, it does so at the expense of a requirement for tighter control over the incident light intensity. Instead, we introduce a new type of exposure system employing a multiplicity of two-photon excitation frequencies, which interfere with one another to produce a superresolution stationary image, exhibiting a true doubling of the spatial resolution.

We can examine the resolution limits by studying the fringe pattern produced by two rays converging from opposite edges of a lens as illustrated in Fig. 1(a). Such a fringe pattern is an indication of the resolution limits. Figure 2(a) shows the intensity fringe pattern in the focal plane that results from two rays of individual wave vector $\boldsymbol{k}$ converging at an angle θ. The spatial period of the fringes is determined by an in-plane wave vector of magnitude $K = 2|k|\sin\theta$. The distribution of intensity, $I(x)$, in the focal plane is simply $I(x) = (1+\cos Kx)$.

Since two-photon absorption is proportional to the square of intensity, the two-photon exposure will be proportional to

$$(1+\cos Kx)^2 = (\tfrac{3}{2} + 2\cos Kx + \tfrac{1}{2}\cos 2Kx), \tag{1}$$

a functional dependence that is plotted in Fig. 2(b). We can see that the fringe pattern of two-photon absorption in Eq. (1) and Fig. 2(b) is a mixture of a normal-resolution image represented by the $\cos Kx$ term and a superresolution image represented by $\cos 2Kx$. The superresolution image at $\cos 2Kx$ consists of spatial harmonics at the wave-vector $2K$, and would represent a doubling of the spatial resolution over ordinary one-photon lithography. Unfortunately the image is a mixture of both resolutions. Our goal in this paper is to show how to enhance the superresolution image, and to suppress the normal-resolution image, to the greatest degree possible.

The exposure of photoresist is usually[7] represented in a graph of fractional resist thickness after development (t/t_0) versus light intensity exposure as in Fig. 3(a). A figure of merit for the photoresist is the photographic contrast or gamma:

$$\gamma_1 \equiv \frac{d(t/t_0)}{d\log_{10} I} \approx \frac{1}{\log_{10}(I_c/I_0)}. \tag{2}$$

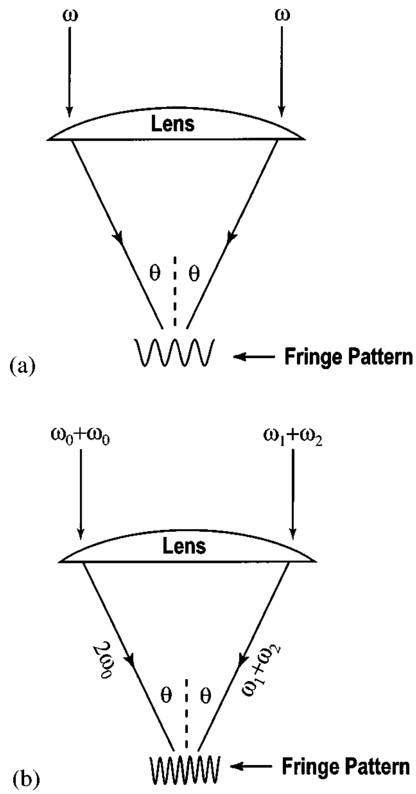

Fig. 1 (a) The intensity fringe pattern produced by rays converging from opposite edges of a lens. (b) The fringe pattern produced by two-photon excitation of a photoresist, in which the incident rays on opposite sides of the lens are separated into distinct frequency groupings. The frequency differences cause normal-resolution fringes to oscillate rapidly in time, and they get washed out.

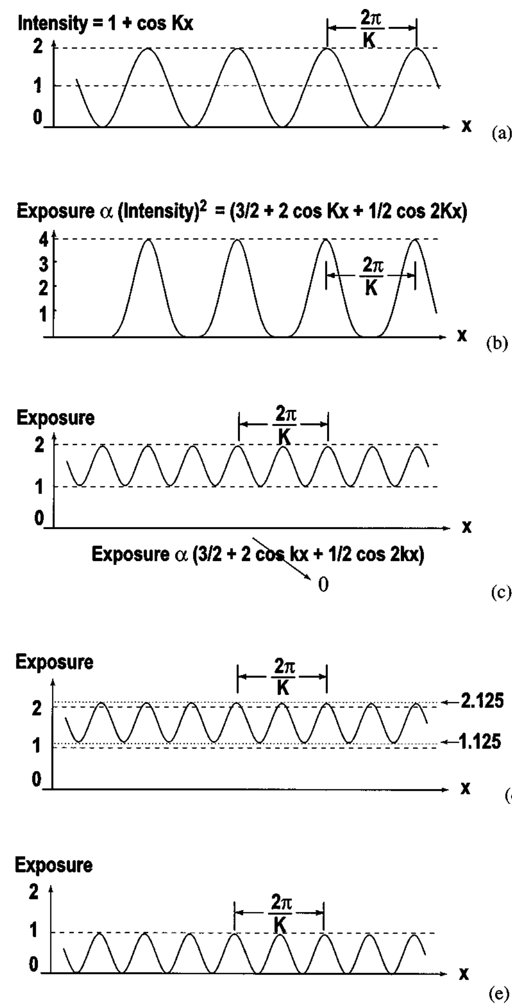

Fig. 2 (a) The ordinary intensity fringe pattern produced by converging rays as in Fig. 1(a), where $K=2k\sin\theta$. (b) The intensity-squared fringe pattern, which consists of a normal-resolution spatial harmonic at K, a superresolution spatial harmonic at $2K$, and a constant term. (c) The effect of canceling the normal-resolution spatial harmonic at K. The superresolution component at $2K$ remains, on a constant background. (d) Using the frequency combinations of Fig. 1(b) actually eliminates the normal-resolution component. (e) By employing a photoresist with a sharp atomic transition at $2\hbar\omega_0$, the constant background is also eliminated, leaving a pure superresolution image.

High contrast is a useful property for a photoresist. In two-photon exposure, the response is proportional to intensity squared. Therefore the argument of the denominator of Eq. (2) is squared and the effective two-photon contrast doubles: $\gamma_2 \rightarrow 2\gamma_1$, which is good. Thus two-photon exposure merely improves the photographic contrast gamma, but, as illustrated in Fig. 3(a), it can never be better than infinite gamma, or an infinitely sharp threshold. Ultimately, even infinite gamma is a poor substitute for actually improving the spatial resolution, because it requires exquisite control over the absolute intensity.

The limited benefits of two-photon exposure are due to the fact that the two-photon image includes both normal-resolution spatial harmonics at K and superresolution spatial harmonics at $2K$, as indicated in Eq. (1). We want the image to contain only the superresolution image at $2K$. If we could somehow eliminate the normal resolution image,[8,9] we would be left with the superresolution image only:

$$\text{exposure} \propto \left(\frac{3}{2} + 2\underbrace{\cos}_{=0} Kx + \frac{1}{2}\cos 2Kx\right), \tag{3}$$

which is plotted as Fig. 2(c). Thus by eliminating the normal-resolution image, the superresolution image would be present on a 50% background, which is tolerable. Nevertheless, we will show in this paper that the background can be entirely eliminated.

The method, or trick, for eliminating the normal resolution image is indicated in Fig. 1(b). The idea is to destroy stationary interference patterns corresponding to the linear image, while maintaining a stationary interference pattern for the superresolution image. Arrange the incident rays to consist of ω_0 on one edge of the lens, and two other frequencies slightly above and below ω_0 (i.e., $\omega_1=\omega_0+\delta$, and $\omega_2=\omega_0-\delta$) on the other edge of the lens, where $2\omega_0=\omega_1+\omega_2$. Fringes resulting from the interference of ω_0 and ω_1 oscillate rapidly at the difference frequency δ, and they wash away, averaging to a uniform background. Thus the normal-resolution image disappears. Provided that the frequencies $2\omega_0$ and $\omega_1+\omega_2$ are coherently related, the superresolution fringes are stationary and they do not wash

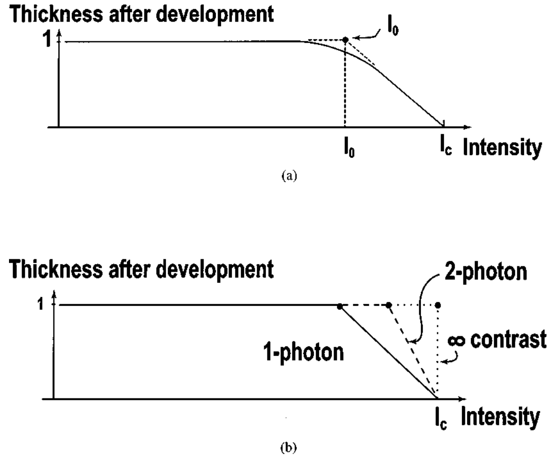

Fig. 3 (a) The fraction of positive photoresist remaining after development under one-photon exposure, contrast≡gamma $\equiv 1/\log_{10}(I_c/I_0)$. (b) Under two-photon exposure the contrast can be twice as steep, but it can never be better than an infinitely sharp exposure threshold.

away. This produces the result indicated in Eq. (3) and in Fig. 2(c).

In a more exact derivation, the two-photon exposure is proportional to the intensity squared of the optical electric field raised to the fourth power, $|\epsilon|^4$, where

$$\epsilon = \epsilon_0 \exp[i(\boldsymbol{k}_0 \cdot \boldsymbol{x} - \omega_0 t)] + \epsilon_1 \exp[i(\boldsymbol{k}_1 \cdot \boldsymbol{x} - \omega_1 t)] + \epsilon_2 \exp[i(\boldsymbol{k}_2 \cdot \boldsymbol{x} - \omega_2 t)] \quad (4)$$

with $\boldsymbol{k}_0$, $\boldsymbol{k}_1$, and $\boldsymbol{k}_2$ the wave vectors of the incident beams. When Eq. (4) is raised to the fourth power, the lower-resolution image with fringes at $\boldsymbol{K} = \boldsymbol{k}_0 - \boldsymbol{k}_1$ oscillates in time at a frequency δ. Thus the normal-resolution image washes out. The superresolution image, with fringes at $2\boldsymbol{K} = 2\boldsymbol{k}_0 - \boldsymbol{k}_1 - \boldsymbol{k}_2$, is stationary in time, since $2\omega_0 = \omega_1 + \omega_2$ (subject however to the requirement for coherence between $2\omega_0$ and $\omega_1 + \omega_2$). Dropping the rapidly oscillating components of the fringe pattern, the stationary image has spatial frequency components only at $2K$. A more exact version of Fig. 2(c) is plotted as Fig. 2(d), showing that the peak-to-valley ratio of the fringes is 1.9 rather than 2. Thus the spatial resolution has actually doubled, but the image sits on a background.

If the photoresist contrast gamma is $> 1/\log_{10}(1.9) \approx 3.6$, the background may be tolerable, but the background can be eliminated in any case, as will be shown later. The background in Fig. 1(b) is due to two-photon interference terms at frequency combinations $\omega_0 + \omega_1$, $\omega_0 + \omega_2$, $2\omega_1$, and $2\omega_2$. None of these interference terms produces a stationary fringe pattern, but they do contribute to the featureless background. Only $2\omega_0$ spatially interferes with $\omega_1 + \omega_2$ to produce a stationary image, which happily occurs at superresolution.

A possible exposure system is shown in Fig. 4. Very short pulses of high peak power are needed to produce a damage-free two-photon exposure in the photoresist. Fortunately such pulses contain a wide spectrum of frequencies that can be used to obtain the different frequency combina-

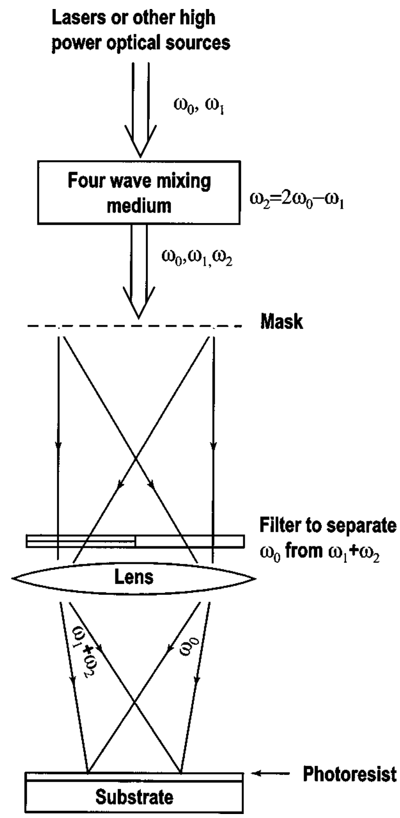

Fig. 4 Layout of a two-photon exposure system. At the top, the short laser pulses and the required optical frequencies are generated. These illuminate a lithographic mask. Near the focusing lens, the different optical frequencies are diverted into different zones on the lens. This ensures that the normal-resolution image will be washed away while the superresolution image remains.

tions. The positive dispersion that will likely occur in the thick lens system needed for high-resolution lithography can be precompensated for by negatively dispersing the pulses before sending them through the system. If additional bandwidth is required, the short pulses can be readily frequency converted to provide new optical frequencies, for example by four-wave mixing as shown in Fig. 4. Such a nonlinear process is relatively efficient due to the high intensity of the short pulses. The various frequencies can illuminate a mask, even a phase mask,[10] as in conventional photolithography, but near the lens the various frequencies become spatially separated by spectral filters. The lens can be divided into zones, some of which pass certain frequency combinations, and some which pass other combinations. For example, in Fig. 4 the lens is divided into two zones, as illustrated in Fig. 5(a) and by the spectral filter function of Fig. 5(b). The frequency ω_0 passes through one zone, and the frequencies ω_1 and ω_2 pass through the other zone. Variations on the optical layout in Fig. 4 are possible, including the insertion of optical gain, various ways of generating ω_0, ω_1, and ω_2, etc. The spectral filters that need to be inserted into the lens system could be thin-film Fabry-Perot filters taking up negligible amounts of space.

Figure 5(c) shows the surface area of the lens divided into four zones, which would require eight different frequencies: $\omega_1 + \omega_2 = \omega_3 + \omega_4 = \omega_6 + \omega_6 = \omega_7 + \omega_8$, subject to the condition that preferably none of the eight frequen-

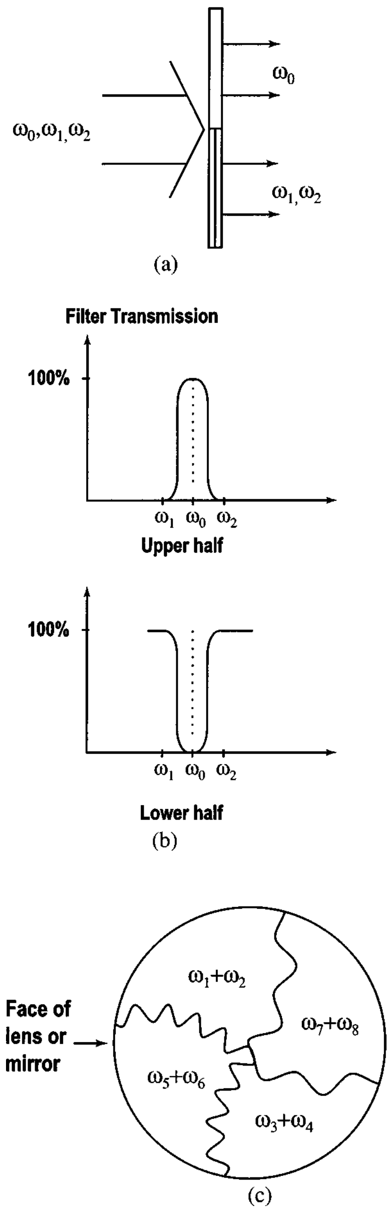

Fig. 5 (a) A spectral filter separates the various optical frequencies of Fig. 1(a) into two zones. (b) An example of the spectral filter function in the two zones. (c) Division of a lens area into four zones. The boundaries between zones may be fuzzily defined.

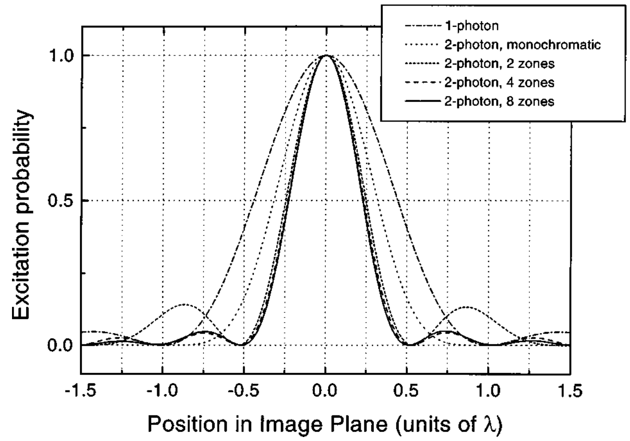

Fig. 6 The dash-dotted line represents the intensity distribution at the focus of a lens obtained by linear diffraction through a numerical aperture of 0.5. The dotted line is the intensity-squared distribution associated with two-photon absorption from a monochromatic beam. The other three curves represent multifrequency two-photon excitation in a photoresist with two, four, and eight zones respectively. Whether for two or eight zones, the resolution is essentially twice as good as for the dash-dotted ordinary one-photon exposure.

cies are equal. Under these circumstances, the individual frequencies may produce low-resolution images which are smeared out by the rapidly oscillating fringes while the superresolution image remains stationary.

If desired, the smeared-out background on which the superresolution image is superimposed can be entirely eliminated. This can be accomplished by arranging for a sufficiently sharp atomic transition at $2\hbar\omega_0$ inside the photoresist. In such a resist the background two-photon transitions at $\omega_0+\omega_1$, $\omega_0+\omega_2$, $2\omega_1$, and $2\omega_2$ in Fig. 1(b) do not occur, and the smeared-out background vanishes. This results in the pure superresolution fringe pattern of Fig. 2(e) at a spatial wave vector of $2\boldsymbol{K}$ with no background, and is the culmination of two-photon lithography. Although currently available photoresists are not designed to exhibit a sharp transition, such resists are conceivable. One way to produce such a resist could be to include an alkaline-earth metal, which is excited by the incident light to an autoionizing state. These transitions are sharp and provide the electron that is needed for the chemical transition upon exposure.

Discrete rays are considered in Fig. 1(b). In a realistic case, however, the incident illumination would cover broad areas of the lens as in Figs. 4 and 5, rather than the discrete rays of Figs. 1 and 2. Therefore it is important to evaluate the effect of broad-area lens illumination, rather than having individual discrete rays forming the image. Figure 6 displays various numerically computed images of a narrow, sharp spatial line source, as limited by the finite numerical aperture (NA) of a lens, treating the problem one-dimensionally. We take in this case NA=0.5, expressing the image size in units of the fundamental wavelength $\lambda \equiv 2\pi c/\omega_0$.

The lowest-resolution image pattern in Fig. 6 represents the ordinary one-photon intensity distribution obtained by linear propagation through the lens. The dotted line is the ordinary two-photon image that might be produced by monochromatic illumination, without taking advantage of multiwavelength illumination as presented in this paper. The two-photon image is narrower than the one-photon image owing to the intensity-squared distribution and the improved effective contrast or gamma.

The next three cases consider a sharp two-photon transition energy, demonstrating the effect of subdividing the lens into either two, four, or eight zones, with each individual zone having a separate frequency combination $\omega_i+\omega_j$. The image is marginally improved when more zones are provided, but the difference in resolution is slight. For the eight-zone case, the spatial resolution is almost exactly twice that of the linear image, as expected. The main difference between two zones and eight zones is that the subsidiary exposure tails are slightly more pronounced when there are two zones. In a fully two-dimensional lens it seems likely that four zones would be adequate in practice.

The results shown were obtained with a single point source. In a real projection system an important question is how faithfully a full pattern is transferred to the image. We are currently investigating this question in full detail. However, it can already be said that the transition from a single point source to a full pattern has to be made cautiously, because of possible cross terms between the fields from different source points.

We have shown that in a two-photon-pumped photoresist exposure system, images can be formed at one-half the normal Rayleigh resolution limit by using a multiplicity of optical pump frequencies.

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