Twofold spatial resolution enhancement by two-photon exposure of photographic film

Dmitriy V. Korobkin
Eli Yablonovitch
University of California, Los Angeles
Electrical Engineering Department
1541 Boelter Hall
Los Angeles, California 90025-1594
E-mail: dkorobkin@sabeus.edu

Abstract. Two-photon absorption of photosensitive media can produce interference fringes with double spatial frequency. This requires the employment of multiple-frequency beams, which interfere with one another to produce a stationary image with double spatial resolution. The required beams were produced by frequency filtering of broadband radiation from a cw mode-locked femtosecond Ti:sapphire laser ($\lambda = 790$ nm) in a dispersion-free pulse shaper. Then the two multifrequency rays converged from opposite edges of a lens, focusing on Kodak commercial film. The laser intensity was high enough to produce a two-photon exposure. The doubling of the spatial frequency of the interference pattern has been observed, but the contrast ratio of the pattern was limited by competition from the more usual one-photon absorption. Laser pulse parameters for a single-pulse two-photon exposure have been estimated.
[DOI: 10.1117/1.1479706]

Subject terms: photolithography; two-photon absorption.

Paper 010178 received May 22, 2001; revised manuscript received Dec. 28, 2001; accepted for publication Jan. 11, 2002.

Computers have been major driving forces of technical revolution. Tremendous progress has been achieved in building faster integrated circuits with increasingly greater density of their elements. The primary tool for transferring circuit images from masks onto substrates is optical lithography. The minimum possible pitch (spacing between elements) is set by the wave nature of light. Particularly, in interferometric lithography,[1] when two beams are made to converge at an angle 2θ [see Fig. 1(a)], interference effects form a set of fringes with a spacing $s = \lambda/(2 \sin \theta)$. When $\theta \rightarrow \pi/2$, the minimum possible pitch goes to $\lambda/2$—the so-called Rayleigh diffraction limit. This is the minimum pitch that can be achieved with linear (single-photon) absorption.[1] Hence, sources with ever shorter wavelength are used to fabricate integrated circuits with smaller features. Current technology employing 248-nm KrF excimer lasers is able to produce 180-nm features; changing to shorter-wavelength (193-nm) ArF lasers will lower the limit to 130 nm.

Recently, experiments on two-photon exposure of photosensitive media (both photoresist and photographic film) have been performed.[2–4] One may ask whether two-photon absorption can be used to overcome the Rayleigh criterion and improve the optical resolution. Consider the fringe pattern produced by two coherent beams of wave vector $\mathbf{k}$ $(k = 2\pi/\lambda)$, converging at angle 2θ [see Fig.1(a)]. The distribution of intensity is given by $I(x) = 1 + \cos Kx$, where $K = 2k \sin \theta$. For the case of one-photon absorption the exposure dose Δ is proportional to the intensity, that is, $\Delta(x) = 1 + \cos Kx$. This is a classical case of two-beam interference [see Fig. 1(b)]. When the absorption mechanism is a two-photon one, the exposure Δ is proportional to the square of the intensity: $(\Delta x) = (1 + \cos Kx)^2 = 3/2 + 2 \cos Kx + 1/2 \cos 2Kx$ [see Fig. 1(c)]. The interference pattern consists of spatial harmonics with both K and $2K$ spatial frequencies. The resulting curve has narrower features than in the classical single-photon case, but the spacing between maxima stays essentially the same: $\lambda/(2 \sin \theta)$.

Recently, Yablonovitch and Vrijen[5] have proposed a new type of exposure arrangement to eliminate the middle term ($2 \cos Kx$) and achieve a true doubling of the spatial resolution. The idea was to destroy the stationary interference pattern corresponding to the linear image, while maintaining the one for the superresolution image. One of the converging beams has to consist of optical frequency ω_0 alone, and the second beam, of frequencies ω_1 and ω_2 such that $\omega_1 = \omega_0 + \delta$ and $\omega_2 = \omega_0 - \delta$, so $2\omega_0 = \omega_1 + \omega_2$ [see Fig. 2(a)]. Fringes resulting from the interference of ω_1 and ω_0 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 ω_0, ω_1, and ω_2 are coherently related, the superresolution fringes are stationary and do not wash away. More extensive theoretical considerations can be found in Ref. 5. The actual fringe pattern from that article is also shown in Fig. 2(b). A slightly different approach utilizing entangled photons, suggested in Ref. 6, also could double the spatial resolution.

The goal of this paper is to experimentally verify the concept initially proposed in Ref. 5. Our choice of two-photon sensitive medium was Kodak commercial film (Catalog No. 198 7874). It is a blue-sensitive material (designed for one-photon absorption between 350 and 480 nm).[7] A typical size of a single grain is 5 to 10 μm. Two-photon exposure of that type of medium has been extensively investigated elsewhere.[2] The radiation source in our

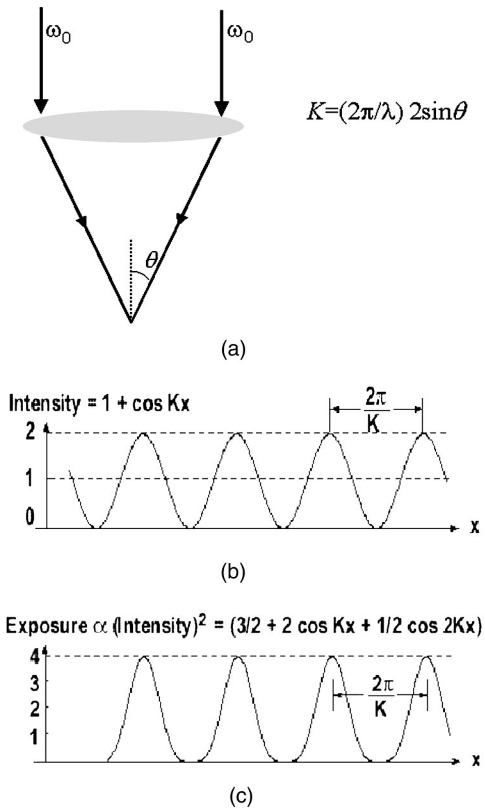

Fig. 1 (a) Classical two-beam interference. (b) One-photon fringe pattern. (c) Two-photon fringe pattern.

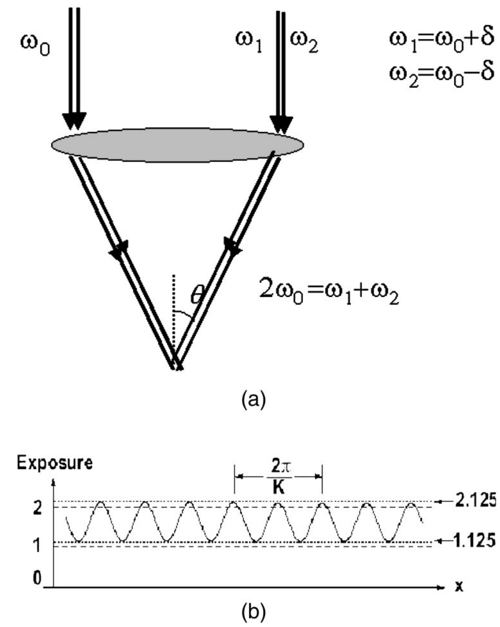

Fig. 2 (a) Multifrequency interference. (b) Fringe pattern for multifrequency interference (from Ref. 5).

experiments was a Ti:sapphire laser system (Spectra-Physics Tsunami) pumped by 10 W of 532-nm radiation from a Millennia X laser. The output parameters of the Ti:sapphire laser were: 80-fs single pulse duration, 82-MHz repetition rate, 0.6-W average output power, 790-nm central wavelength. To make sure that only 790-nm radiation was present in the output beam and to cut off possible blue and green light, a RG color filter was placed near the laser output. Single-pulse parameters at the output of the system were ≈ 7-nJ energy and 90-kW peak power. The total exposure time was controlled by a combination of an electro-optic (Pockels cell) and a mechanical shutter. The electro-optic shutter made it possible to achieve nanosecond switching times; however, its contrast ratio was limited to 1:200. To make sure that no undesirable radiation was leaking from the laser, an electromechanical shutter (2-ms minimum window) was placed after the Pockels cell. The two shutters were synchronized with a Stanford Research digital delay generator (model DG535). All experiments were performed in a darkened room. An additional small chamber $(20\times 20\times 20\ \text{cm})$ protected the film from stray light. The exposed film was processed according to Kodak specification.[7]

The experiment can be divided into two parts. In first we measured the one- and two-photon absorption parameters of the film. Also we made sure that the radiation intensity of our laser system was strong enough to induce predominantly two-photon exposure of the medium, so we could proceed to the second part—to produce a multifrequency interference pattern.

Due to group velocity dispersion (GVD) inside the Pockels cell, the initial 80-fs pulses were stretched to ≈ 600 fs. These broadened pulses were recompressed to the original 80 fs by a conventional prism-pair compressor.[8] Then the output beam (average power $P_{av}=0.6$ W, peak power $P_{peak}=90$ kW) was focused onto a $400\times 250\ \mu\text{m}$ spot (area $S=10^{-3}\ \text{cm}^2$) by 1-m lens, and calibrated exposures were made. It turned out that the film saturation occurred at a total exposure time greater than 20 μs. Then we intentionally destroyed the mode-locked mode of operation of the Ti:sapphire system, making it cw (at the same average output power) and repeated the measurements. Thereupon the saturation occurred only after 100 μs of total exposure time.

For one-photon absorption the probability $P^{(1)} \sim \sigma^{(1)} I \tau n$, where $\sigma^{(1)}$ is the cross section of one-photon absorption, I the peak intensity, τ the pulse duration, and n the number of absorbed pulses. This can be rewritten as $P^{(1)} \sim \sigma^{(1)} E_{\text{total}}$, where E_{total} is the density of total absorbed energy. In saturation, $P^{(1)} \rightarrow 1$, and E_{total} reaches its saturation value $(E_{\text{total}})^{(1)}_{\text{sat}}$. In our case the total absorbed energy at exposure time $\tau_{\text{exp}}=100\ \mu\text{s}$ was $P_{av}\tau_{\text{exp}}/S = (E_{\text{total}})^{(1)}_{\text{sat}} = 60\ \text{mJ/cm}^2$. For comparison, at the peak of the absorption curve (350 nm) the one-photon sensitivity of the film is $\sim 1\ \mu\text{J/cm}^2$.[2] For the case of two-photon absorption its probability is $P^{(2)} \sim \sigma^{(2)} I^2 \tau n$, where $\sigma^{(2)}$ is the cross section for two-photon absorption. This expression also can be simplified, to $P^{(2)} = \sigma^{(2)} I E_{\text{total}}$. In that case the saturation parameter is the product of total absorbed energy E_{total} and the peak intensity I of the single pulse. In our experiment it was $P_{\text{peak}} P_{av} \tau_{\text{exp}} / S^2 = E_{\text{total}} I = 1.1\times 10^6\ \text{JW/cm}^4$.

Our next step was to build a multifrequency interferometer. The experimental setup is shown in Fig. 3. The backbone of the system is a dispersion-free pulse-shaping

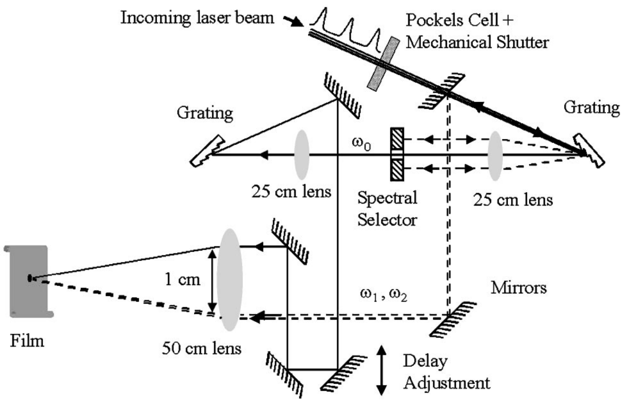

Fig. 3 Experimental setup.

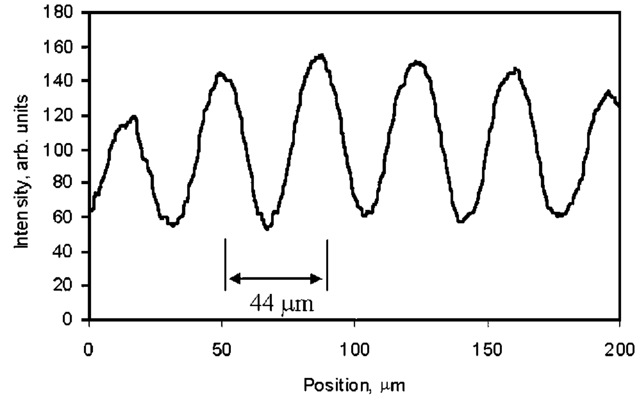

Fig. 5 Intensity profile of ordinary interference pattern.

apparatus.[9] The broadband radiation from the femtosecond Ti:sapphire laser was reflected by a diffraction grating (1200 lines/mm) through the positive lens (25-cm focus), toward a spectral selector (a mirror with a 3.5-mm hole at the center). The central part of the spectrum passed through the hole, then through the second lens (also 25-cm focus), and finally was recombined into a collimated beam by the second grating (also 1200 lines/mm). The edge portions of the spectrum were reflected back and were recombined into a collimated beam by the first grating. The spectral selector was slightly tilted, which allowed us to separate the reflected and incoming beams. The transmitted beam consisted of the radiation with frequency ω_0 and the reflected radiation with frequencies ω_1 and ω_2. The position and the diameter of the central hole were chosen such that $2\omega_0 = \omega_1 + \omega_2$ and the average power in the two arms was equal. The distance between the gratings and the lenses was adjusted such a way that the initial pulse chirp induced by the Pockels cell was compensated. An extra delay line was used to match the time delays in the two arms.

The optical spectrum after passage through the system is shown in Fig. 4. Since we limited the spectral bandwidth in both arms, the corresponding pulses were inevitably broader ($\approx$200 fs each). The average intensity in each arm was 100 mW. The two beams were made parallel (1 cm between them) and then focused onto a single spot ($250 \times 150\ \mu$m) by a 50-cm lens. The initial distance between the interfering beams and the focal length of the final lens were chosen such a way that the period of the classical interference pattern would be at least 4 times larger than the typical grain size of the film. The fine adjustment of the delay line was made by inserting a nonlinear crystal at the beam intersection and getting a maximum signal of cross-generated second harmonics.

All optical elements of the system inevitably decrease the spatial coherence of the radiation, so auxiliary tests to obtain regular interference fringes were performed. We replaced the spectral selector with an ordinary 50% reflection mirror and made calibrated exposures (so-called system test). Since no spectral selection was involved, the pulse duration in those tests was 80 fs. Figure 5 shows the intensity profile averaged along the fringes over $\approx$20 grain sizes. One can see a set of well-defined interference fringes with 44-μm period. The spatial coherence of the beam was found to be good enough to create classical interference fringes with a 50-cm final focusing lens, so we could proceed with multifrequency exposures. Also, the absence of half-period features indicated that no second-harmonic radiation was generated inside the system.

The frequency selector was reinstalled, and calibrated exposures were taken. Figure 6 shows the intensity profile of the pattern at 5-μs exposure time. The other experimental parameters were: total absorbed energy $E_{\mathrm{total}} = 2.7\ \mathrm{mJ/cm^2}$, peak intensity $I_{\mathrm{peak}} = 3.2\times10^7\ \mathrm{W/cm^2}$, $I_{\mathrm{peak}}E_{\mathrm{total}} = 8.6\times10^4\ \mathrm{WJ/cm^4}$. One can see a set of major and minor maxima. The distance between major maxima (44 μm) corresponds to the classical interference spacing. The presence of the minor maxima indicates the doubling

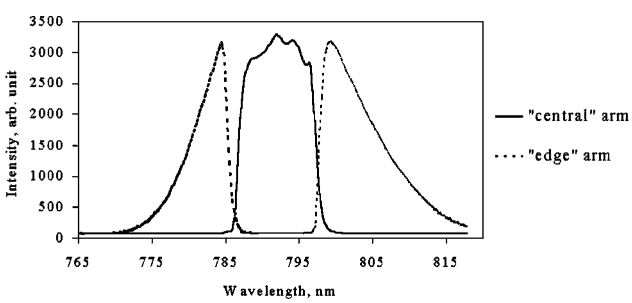

Fig. 4 Spectral characteristics of the interferometer.

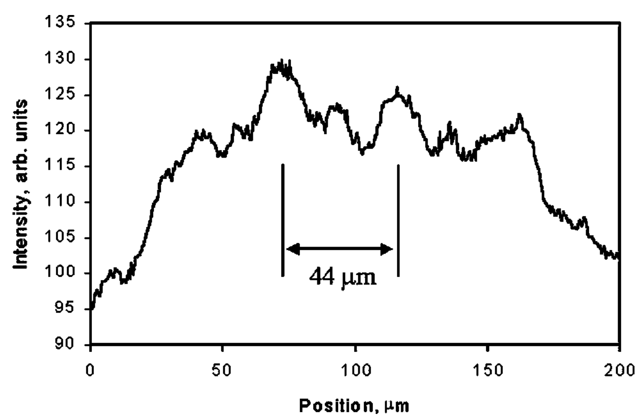

Fig. 6 Intensity profile of multifrequency interference pattern.

of spatial frequency due to two-photon absorption. The maximum possible value of the contrast (ratio of maximum to minimum intensity) in this configuration is 1.89. In our case it is close to 1.07. Such a small value of the contrast probably occurs because the one- and two-photon effects are in fact comparable to each other. Indeed, estimates show that two-photon absorption is only 1.6 times stronger than single-photon.

To achieve higher intensities, we replaced the 50-cm final focusing lens with a 25-cm one and correspondingly decreased the initial distance between arms to 0.5 cm. When we performed the system test (no spectral filtration, same-frequency beams), instead of observing regular classical fringes, we obtained no interference pattern at all. Changing to the multifrequency setup did not produce an interference pattern either. We have no satisfactory explanation of the failure. One of the reasons could be insufficient spatial coherence of the radiation. Also, insufficient coherence could be one of the reasons for the low contrast in the case of the 50-cm lens.

It is more advantageous to use a low-repetition-rate high-power system similar to one described in Ref. 2. The total absorbed energy E_{total} could be kept well below saturation level for single-photon absorption, whereas the exposure of the film would be achieved by a single pulse due to two-photon absorption. One can estimate that for a 1-ps pulse focused onto a 1×1-mm spot, its energy should be in the range 20 to 50 μJ to achieve predominant two-photon exposure. That can be easily provided by a Ti:sapphire amplifier.

In conclusion, we have experimentally demonstrated a doubling of spatial frequency of the interference pattern using two-photon absorption by Kodak commercial film. The interference pattern was formed by two multiple-frequency beams, which interfere with one another to produce a stationary image with double spatial resolution. In order to create the multifrequency beams with suitable parameters, we performed a frequency filtering of broadband radiation from a mode-locked femtosecond cw Ti:sapphire laser in a dispersion-free pulse shaper. The intensity of the beams was high enough to produce a two-photon exposure. However, insufficient spatial coherence of the radiation and the competition from single-photon processes prevented us from achieving the maximum possible contrast ratio. We also have estimated the parameters of a laser system to achieve a two-photon exposure with a single laser pulse.

Acknowledgment

We would like to thank Dr. R. Vrijen for helpful discussions. This work is supported by the Army Research Office, DAAD19-99-1-0196.

References

1. S. R. J. Brueck, S. H. Zaidi, X. Chen, and Z. Zhang, "Interferometric lithography—from periodic arrays to arbitrary patterns," *Microelectron. Eng.* **41/42**, 145–148 (1998).
2. P.-W. Wu, B. Dunn, E. Yablonovitch, V. Doan, and B. Schwartz, "Two-photon exposure of photographic film," *J. Opt. Soc. Am. B* **16**, 605–608 (1999).
3. S. Maruo, O. Nakamura, and S. Kawata, "Three-dimensional microfabrication with two-photon-absorbed photopolymerization," *Opt. Lett.* **22**, 132–134 (1997).
4. G. Witzgall, R. Vrijen, E. Yablonovitch, V. Doan, and B. J. Schwartz, "Single-shot two-photon exposure of commercial photoresist for the production of three-dimensional structures," *Opt. Lett.* **23**, 1745–1747 (1998).
5. E. Yablonovitch and R. Vrijen, "Optical projection lithography at half the Rayleigh resolution limit by two-photon exposure," *Opt. Eng.* **38**, 334–338 (1999).
6. A. N. Boto, P. Kok, D. S. Abrams, S. L. Braunstein, C. P. Williams, and J. P. Dowling, "Quantum interferometric optical lithography: exploiting entanglement to beat the diffraction limit," *Phys. Rev. Lett.* **85**, 2733–2736 (2000).
7. Kodak Commercial Film, Kodak technical data publication F-16, Eastman Kodak, Rochester, NY.
8. R. L. Fork, O. E. Martinez, and J. P. Gordon, "Negative dispersion using pairs of prisms," *Opt. Lett.* **9**, 150–152 (1984).
9. A. M. Weiner, J. P. Heritage, and E. M. Kirschner, "High-resolution femtosecond pulse shaping," *J. Opt. Soc. Am. B* **5**, 1563–1572 (1988).

Dmitriy V. Korobkin received the engineer-scientist degree from Moscow Institute of Physics and Technology in 1988 and the PhD from Princeton University in 1999. He is currently a visiting assistant researcher at the University of California, Los Angeles. His research interests include laser physics, nonlinear optics, and optical lithography.

Eli Yablonovitch is a professor of electrical engineering at UCLA and the director of the UCLA Nanoelectronics Laboratory. He received his PhD in applied physics at Harvard University in 1972. Currently he is working mainly on epitaxial liftoff technology, photonic band structure, and optical code division multiplexing. He was at Bell Telephone Laboratories for two years, became a professor of applied physics at Harvard, and in 1979 joined Exxon to do research on photovoltaic solar energy. Then, in 1984, he joined Bell Communications Research, where he was a Distinguished Member of Staff, and eventually Director of Solid-State Physics Research, staying until 1992. Among his honors are an Alfred P. Sloan fellowship (1978-1979), the Adolf Lomb Medal of OSA (1978), an R&D 100 award (1990), the W. Streifer Scientific Achievement Award of IEEE/LEOS (1993), and the R. W. Wood Prize of OSA (1996). He has been named a fellow of IEEE (1992), APS (1990), and OSA (1982), and is a member of Eta Kappa Nu.