# Two-photon exposure of photographic film

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Photographic film has commonly been exposed by a single-photon absorption mechanism. We determine the conditions for film exposure by direct two-photon absorption. Using subpicosecond laser pulses, we find that two-photon exposure for commercial film has a threshold fluence and an intensity of 0.0008 J/cm$^2$ and 0.0066 TW/cm$^2$, respectively, well below the optical damage threshold. Multiphoton photography has the potential for higher spatial resolution and affords an opportunity for three-dimensional image storage. © 1999 Optical Society of America [S0740-3224(99)00304-5]

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Since the discovery of photography in 1837,[1] the light absorption leading to image formation has always been through single-photon excitation of the photographic medium. Recent developments in ultrafast laser technology have now made two-photon absorption, which requires high peak power, a practical exposure mechanism. For a long time it has been possible to attain peak intensities of $\approx 10^{13}$ W/cm$^2$, but with subpicosecond pulses peak intensities can now be attained at fluences of $\ll 1$ J/cm$^2$, safely below the damage threshold of many materials. Thus we can have a high probability of two-photon exposure without burning or damaging the photographic film.

In a two-photon exposure mechanism there is the potential for improved spatial resolution compared with the normal Rayleigh limit. Two-photon absorption uses the square of the pulse intensity profile, resulting in a $\sqrt{2}$ decrease in the spot size (FWHM), assuming Gaussian optics. More important, Yablonovitch and Vrijen recently introduced a new type of exposure system that employs a multiplicity of two-photon excitation frequencies that interfere with one another to produce an ultraresolution stationary image, exhibiting a true doubling of the spatial resolution.[2] In addition, multiphoton exposure with high-numerical-aperture lenses leads to three-dimensional control over the exposure plane and the possibility of three-dimensional photographic storage and patterning.[3] Given all these potential advantages, it is surprising that to date no effort has been made to investigate the possibility of two-photon photography.

Photographic media are photosensitive emulsions based on silver halides. For photographic film to serve as a two-photon recording medium, there must be a two-photon transition (spectrally isolated from the one-photon transition) that can initiate the photographic process. Prior work on two-photon absorption in AgCl has demonstrated an allowed–allowed-type transition for two-photon energies near the bandgap and an allowed–forbidden-type transition for energies far from the bandgap.[4] The two-photon absorption coefficient near 4.1 eV has been measured as $1.25 \times 10^{-4}$ cm/MW, within a factor of 5 of theoretical predictions of $2 \times 10^{-5}$ cm/MW.[5] Thus standard photographic film could serve as a recording medium for two-photon processes as well as one-photon processes if (1) the two-photon transition in the silver halides leads to the same electron–hole pair formation and subsequent reduction process as the corresponding one-photon transition and (2) the two-photon transition can be sufficiently excited to produce image formation at pulse energies below the damage threshold of the medium. In this paper we show that both commercial film and photographic paper meet these two requirements, and we demonstrate the first visual recording of images produced by a two-photon (or multiphoton) process.

The photon source used for these experiments is a regeneratively amplified Ti:sapphire laser that produces ~120-fs transform-limited pulses centered at 800 nm with 1 mJ of energy at a 1-kHz repetition rate with a slightly elliptical ($4 \times 5$ mm) beam spot (spectra physics). Control of pulse energy was achieved by attenuation with calibrated neutral-density filters (Melles Griot). The pulse intensity was also varied by our chirping the pulses from 120 to 240 fs by intentional misalignment of the pulse compressor optics. Pulse widths were measured with a single-shot autocorrelator (positive light). The laser pulses passed through a color filter that is

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transmissive at 800 nm but that has an optical density greater than 7 at 400 nm to ensure that no one-photon exposure of the film samples occurred because of residual second-harmonic light in the beam.

We chose to explore the two-photon recording ability of two different commercial photographic media based on silver halides, a film (Kodak catalog no. 198 7894)[6] and a paper (Kodak AZO catalog no. 142 0207).[7] Both are blue sensitive (designed for one-photon absorption between 350 and 480 nm), readily available, monochrome photographic media that (as verified in our laboratory) produce no one-photon images following exposure to light of wavelengths $\geqslant$620 nm. Two-photon exposure experiments were performed in a darkened room. The laser pulses were focused at a fixed position in space to a near-diffraction-limited elliptical spot (FWHM of $\sim$100 $\times$ 120 $\mu$m) with a 1-m focal-length lens. The photographic medium, mounted on a sample holder, was drawn quickly past the focused spot, as illustrated schematically in Fig. 1(a). After exposure, the media were developed in a darkroom with commercial processing products for the developer, stop, and fixer solutions. The details of our processing procedure are summarized in Table 1.

Laser spot image sizes were measured with an optical micrograph of the developed film, such as the one shown in Fig. 1(b), and recorded as the average of the long and the short axes of the slightly elliptical spot pattern. The threshold intensity for image formation was determined by visual inspection of the micrograph with an optical microscope.

The ability of film and photographic paper to record two-photon processes was tested by our exposing the media to femtosecond laser pulses of varying intensity. Laser damage of the media began to occur at fluence levels higher than 0.5 J/cm$^2$, as evidenced by formation of a hole in the center of the image. The magnitude of the observed damage fluence is consistent with reported work for both organic and inorganic materials.[8] As a result all the laser exposure experiments reported below were conducted with a fluence level below 0.4 J/cm$^2$.

The photographic media chosen for our experiments are blue sensitive; for 800-nm photons, they cannot be exposed by a one-photon process, but they should be sensitive to two-photon processes that are equivalent in energy to absorption of a single 400-nm photon. A spectral sensitivity curve that identifies the one-photon exposure fluence for the AZO photographic paper between 350 and 470 nm, adapted from a Kodak publication,[7] is provided in Fig. 2. The sensitivity is defined as the reciprocal of the minimum exposure fluence (joules per square centimeter) to produce a given contrast in the media under fixed development conditions.[7] The photographic paper requires a minimum fluence of $2.8 \times 10^{-6}$ J/cm$^2$ for exposure at 350 nm, and the threshold for exposure increases to $3.8 \times 10^{-4}$ J/cm$^2$ at 470 nm. Extrapolation of the sensitivity curve to 800 nm leads to an estimated one-photon exposure fluence close to $10^9$ J/cm$^2$ for the AZO photographic paper. (The spectral sensitivity for the commercial film is not available, but is expected to be similar to that of AZO paper with a slight shift to higher sensitivity.) In contrast, the exposure fluence per pulse used in the experiments reported here was always kept below 0.4 J/cm$^2$. Thus, even though the extrapolated sensitivity at 800 nm is likely off by several orders of magnitude, it is reasonable to exclude the possibility that the image produced on the AZO paper is caused by a one-photon process.

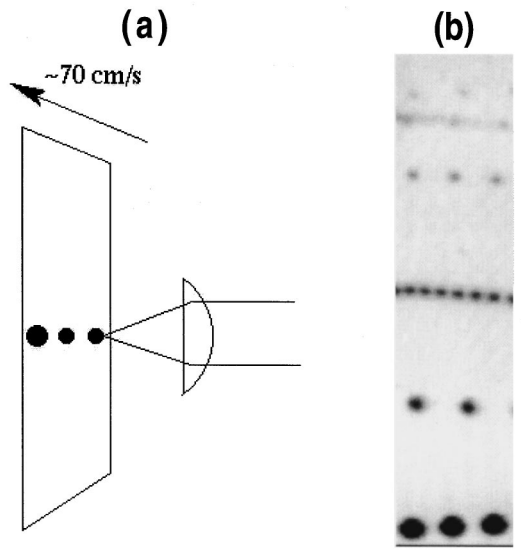


Fig. 1. Schematic illustration of (a) the laser exposure experiment and (b) the resultant film after development.

**Table 1. Processing Steps Involved in Developing Film and Photographic Paper**

| | Developer (s) | Indicator Stop Bath (s) | Fixer (min) | Washing in Water (min) |
|---|---|---|---|---|
| Commercial film | 20[a] | 30[b] | 30[c] | 30 |
| Commercial film | 40[a] | 60[b] | 30[c] | 30 |
| AZO paper | 45[d] | 15[b] | 5[c] | 10 |

[a] Kodak HCl 10, diluted with water in a 1:3 ratio.
[b] Kodak stop bath indicator, prepared as directed in normal working strength.
[c] Kodak fixer, prepared as directed in normal working strength.
[d] Kodak Dektol Developer, diluted with water in a 1:2 ratio.

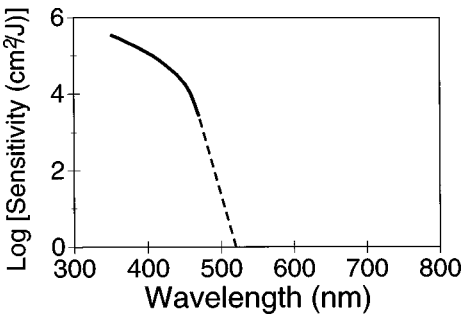


Fig. 2. One-photon spectral sensitivity curve for AZO paper (solid curve, adapted from Ref. 7) and extrapolation toward wavelengths used for two-photon exposure (dashed curve).

Evidence that the images are produced by a two-photon process is provided by experiments that use chirped laser pulses. The film was exposed to both transform-limited (120 fs) and temporally stretched (240 fs) light pulses

with the same energy and spot size (fluence). For two-photon processes, the absorption rate is proportional to $I^2 = (F/\tau)^2$, where $I$, $F$, $\tau$ are intensity (watts per square centimeter), fluence (joules per square centimeter), and pulse width (seconds). For pulses with the same fluence but with pulse widths varying by a factor of 2, the two-photon absorption rate should change by a factor of 4, leading to marked changes in the measured image size as well as the threshold fluence and intensity.

Figure 3 compares the image size produced by pulses with the same energy but two different pulse widths (120 and 240 fs) for a development time of 20 s. The image size of the spots for both pulse widths approaches a saturation value of 450 $\mu$m at high pulse energies, while at low pulse energies near threshold the image size decreases to smaller than 100 $\mu$m. The 240-fs laser pulses, however, produce smaller image sizes compared with the 120-fs pulses of the same energy. In addition, a spot size near threshold of 80 $\mu$m requires a fluence level four times higher for the longer pulses than that for the shorter pulses, as is expected for two-photon absorption. If the exposure were due to a one-photon process, the image size should not demonstrate any dependence on pulse width for the same fluence level, providing confirmation that the photographic film is being exposed by two-photon excitation processes.

Figure 4 shows the effect of laser intensity on two-photon image size for both commercial film and AZO photographic paper. With a developing time of either 20 or 40 seconds, the laser spot image size reaches a saturation value of roughly 450 $\mu$m in diameter. Exposure with higher intensities does not further increase the laser spot image size and eventually results in laser damage to the film. At low intensities away from this saturation regime, the laser spot image size decreases with intensity to values smaller than the ~130 $\mu$m ($1/e^2$) diameter of the focused laser beam. The threshold fluence and intensity for appearance of a two-photon image with 20-s development time are 0.003 J/cm$^2$ and 0.025 TW/cm$^2$, respectively. An image whose size is smaller than the beam spot occurs only at intensities approaching this threshold value. That result occurs because at low pulse energies only the center of the roughly Gaussian-profile laser beam can achieve sufficient intensity to induce the required two-photon absorption; thus multiphoton photography allows the direct production of images that are smaller than the diffraction limit. The saturation size of 450 $\mu$m at high intensities likely arises from "overexposure."

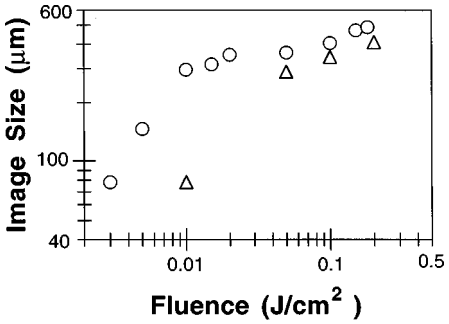


Fig. 3. Effect of pulse duration on the laser spot image size for film after 20-s development (○, 120-fs pulses; Δ, 240-fs pulses).

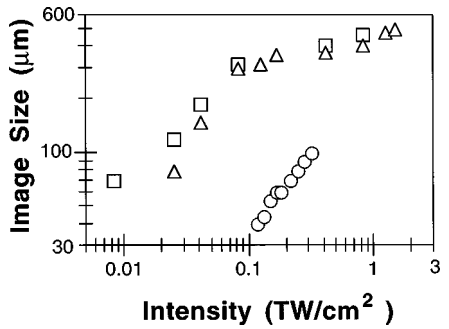


Fig. 4. Effect of intensity and development time on the laser spot image size for 120-fs laser pulses (Δ, film with 20 s in developing solution: □, film with 40 s in developing solution; ○ AZO photographic paper).

Results of the experiment, performed identically but for an extended developing process (40 s), are also shown in Fig. 4. The dependence of image size on laser intensity is the same as for the 20-s development time. Two notable differences, however, are the overall size of the image and the threshold value. The 40-s development time produces larger images for the same pulse intensity. Moreover, the image formation threshold for the longer development time becomes smaller: The fluence and the intensity for spot appearance due to two-photon exposure are 0.0008 J/cm$^2$ and 0.0066 TW/cm$^2$, respectively. These results indicate that, with a longer developing time, latent two-photon images produced by lower-intensity laser pulses can be developed into visible images, effectively reducing the threshold.

Also plotted in Fig. 4 is the image size produced on the AZO photographic paper after exposure and development. The data establish that the two-photon sensitivity of the photographic paper is smaller than that for photographic film at the same intensity, a result consistent with the known one-photon (blue) sensitivities of these media. Thus two-photon images exposed at desired thresholds can be recorded by the appropriate choice of photographic medium and development time.

In summary, this study presents an experimental demonstration of the exposure of photographic film and paper entirely by a two-photon process. A high-intensity laser pulse exposure leads to image formation in these media at wavelengths and fluences at which one-photon processes cannot produce images. The commercial films used are not specifically designed for two-photon work; presumably, new materials optimized for such use would provide even better contrast at lower exposure intensities. With such films multiphoton photography should open new directions for imaging. Spatial resolution can potentially be doubled by the use of two-photon absorption.[2] Multiphoton exposure also provides an opportunity to achieve three-dimensional storage or patterning.[3] Focusing short pulses of light that carry an image into a thick multiphoton recording medium with a high-numerical-aperture lens will lead to absorption only within the focal plane. By scanning the focal plane through the thickness of the material, a series or sequence of multiphoton-produced images can be recorded. This process represents an exciting direction that is simply not possible with conventional one-photon absorption in which all the light is absorbed at the surface of the recording medium.

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