

Pump–probe spectroscopy on photoinitiators for stimulated-emission-depletion optical lithography

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We report on femtosecond pump–probe experiments on two different photoinitiators in solution. These two molecules have recently appeared as attractive candidates for far-field optical lithography based on stimulated-emission-depletion (STED) inspired approaches aiming at beating Abbe's diffraction limit. For the case of 7-diethylamino-3-thenoylcoumarin (DETC), we find that stimulated emission clearly dominates over excited-state absorption, whereas the opposite holds true for the case of isopropylthioxanthone. We argue that it is desirable that stimulated emission dominates over excited-state absorption as depletion mechanism in STED photoresists. Thus, DETC is an attractive corresponding photoinitiator. © 2011 Optical Society of America

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Stimulated-emission-depletion (STED) fluorescence microscopy [1] has circumvented Abbe's diffraction limitation in microscopy by a large margin. Record spatial resolutions down to 5.6 nm have been achieved for visible light [2]. It would obviously be highly interesting to translate this success from optical microscopy to optical lithography. Three groups have recently published corresponding results [3–5]. Two of these have assigned their results to mechanisms other than stimulated emission (SE) [3,4], whereas we have found results that are consistent with SE [5]. However, from a lithography experiment alone, it is very difficult if not impossible to unambiguously rule out other mechanisms. So far, we have successfully used two different photo-deactivatable photoinitiator molecules, namely isopropylthioxanthone (ITX) [5] and 7-diethylamino-3-thenoylcoumarin (DETC) [6] in our lithography experiments. In this Letter, we present femtosecond pump-probe experiments to clarify whether or not SE plays a key role for these two photoinitiators in ethanol solution.

We have previously selected these photoinitiators from a plethora of possibilities because their optical transition wavelengths match that of readily available laser systems and because they exhibit pronounced $S_0 - S_1$ transitions with large oscillator strengths, enabling efficient SE. In this Letter we determine a peak molar decadic extinction coefficient of $930 \text{ L mol}^{-1} \text{ cm}^{-1}$ for ITX and $40550 \text{ L mol}^{-1} \text{ cm}^{-1}$ for DETC. The latter is comparable to that of state-of-the-art fluorescent dyes (e.g., Atto 425 with $45000 \text{ L mol}^{-1} \text{ cm}^{-1}$, see www.atto-tec.com). For comparison, usual photoinitiator molecules (e.g., Irgacure 907 [7]), have values of around $100\text{--}200 \text{ L mol}^{-1} \text{ cm}^{-1}$ for the $S_0 - S_1$ transition, while their $S_0 - S_n$ transitions are often very pronounced. Let us briefly discuss the importance of SE for STED-inspired lithography.

Figure 1(a) schematically depicts the relevant states and transitions of a photoinitiator molecule. A first laser excites photoinitiator molecules from their ground states

to an electronically and vibrationally excited level S_1^* . Some molecules can directly decay to the ground-state nonradiatively. A major fraction of the molecules will relax to an intermediate state S_1 from which they can either fluoresce or undergo intersystem crossing (ISC) to the triplet state T_1 , from where a chemical reaction may be initiated in the actual photoresist. The idea of STED is to bring the molecules from the intermediate state back to the ground state via SE induced by a depletion laser. However, when exposing excited molecules to such a laser beam, SE competes with excitation into higher-energy levels via excited-state absorption (ESA) from S_1 . The behavior of such highly excited molecules is difficult to predict and to control. ESA can be an alternative channel for an effective depletion of the S_1 state, provided that highly excited molecules can relax to the ground state nonradiatively. However, such molecules are often very reactive and their transition rates to the triplet states are often enhanced, both potentially leading to unwanted polymerization. The molecule might also return to the S_1 state nonradiatively and get re-excited several times, thus effectively injecting unwanted heat into the system. Within a photoresist, this temperature change could influence the photoinitiator's transition properties or the polymerization dynamics. Even if this led to an effective suppression of polymerization, this effect would not be suitable for the fabrication of super-resolving features due to the slow and diffusive nature of heat transport. We conclude that SE with the least possible ESA [3] is the preferable depletion mechanism in STED-inspired lithography.

Obviously, the pump-probe contributions of these two processes are distinct: Upon optical pumping, a probe beam experiences a reduced optical density (OD) in case of SE, whereas it experiences an increased OD in case of ESA. Moreover, a negative pump-induced change of the OD, $\Delta\text{OD} < 0$, in a spectral region with negligible ground-state absorption directly indicates SE. However,

a positive signal $\Delta OD > 0$ does not exclude the presence of SE per se, but it does indicate that ESA overcompensates possible SE at this wavelength. In addition to the sign of the pump-probe signal and its spectral signature, its temporal decay provides us with further information that is relevant for using the photoinitiator in an actual photoresist. In particular, such data indicate the optimum pulse durations and the optimal timing between excitation and depletion in the case of pulsed excitation and pulsed depletion.

To allow for direct comparison, Figs. 2(a) and 3(a) depict the known fluorescence and extinction spectra of ITX and of DETC, respectively, in ethanol solution.

In our femtosecond pump-probe experiments, a Clark 2210 laser system is used with a repetition rate of 1 kHz, a central wavelength of 775 nm, a typical pulse duration of 150 fs and an energy of 2 mJ/pulse. A small portion is used for second-harmonic generation, which serves as pump pulses at 387.5 nm. Probe pulses with a duration of <40 fs are generated by a noncollinear optical parametric amplifier and tuned between 473 nm and 900 nm. They are delayed via a translation stage. Pump (probe) pulses are collimated to a diameter of 3 mm (1 mm) at the sample position to ensure homogeneous excitation conditions. The samples are prepared as ethanol solutions in 1 mm fused silica cuvettes with an OD of 0.3 at the excitation wavelength [$c = 2.2 \cdot 10^{-4}$ mol/L (DETC), $c = 3.8 \cdot 10^{-3}$ mol/L (ITX)]. The pump intensity is kept at $1.7 \cdot 10^8$ W/cm² to ensure that only small changes in OD occur. The experiments are performed for both parallel (ΔOD_{\parallel}) and for orthogonal (ΔOD_{\perp}) linear polarization of pump and probe pulses. To separate the aspects of orientation and population dynamics, we compute the “magic-angle” data from these two measurements, i.e.,

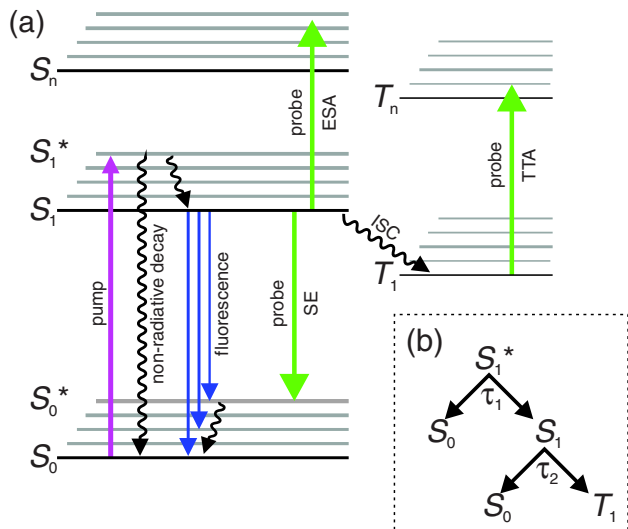


Fig. 1. (a) Scheme of transitions in a photoinitiator molecule for STED optical lithography. Pump laser photons (pink) excite molecules from the S_0 ground state into an excited state S_1^* . After vibrational relaxation to the S_1 state, probe photons (green) can bring the molecule back to its ground state via SE or into yet higher-energy states via ESA. After ISC to the triplet state T_1 , TTA of probe photons may occur. (b) Simple rate-equation model for analyzing the experimental data. The time constants τ_1 and τ_2 describe the population of S_1^* and S_1 , respectively.

$\Delta OD = (\Delta OD_{\parallel} + 2\Delta OD_{\perp})/3$ (see Ref. [8]), and the pump-induced transient anisotropy (see Ref. [9]), $r(t) = (\Delta OD_{\parallel} - \Delta OD_{\perp})/(\Delta OD_{\parallel} + 2\Delta OD_{\perp})$.

The time-resolved pump-probe data for ITX are shown in Fig. 2(c), those for DETC in Fig. 3(c). Obviously, the two behave rather differently. For ITX, the signals are mostly positive, whereas they are largely negative for DETC. For example, at 532 nm probe wavelength, where our recent lithography experiments have been performed [5,6], the (unpumped) optical extinction is close to zero [see Fig. 3(a)]. Thus, these negative ΔOD signals indicate SE. Upon variation of the probe wavelength, the SE roughly follows the shape of the fluorescence spectrum. This indicates small contributions of ESA, which is desirable for efficient STED. Deviations from this simple picture occur for short probe wavelengths where depletion of the ground-state molecules also contributes to negative signals. The overall timescale is a few nanoseconds for ITX and about 100 ps for DETC.

To derive more quantitative temporal information from these pump-probe data, we compare them to a simple rate-equation model derived from the scheme in Fig. 1(b). Upon optical excitation, the S_1^* population quickly decays with time constant τ_1 . A minor contribution to this decay is nonradiative decay back to the ground state. The majority of the molecules relax toward the S_1 state. Thus, both SE and ESA will show a rise with this time constant. A second

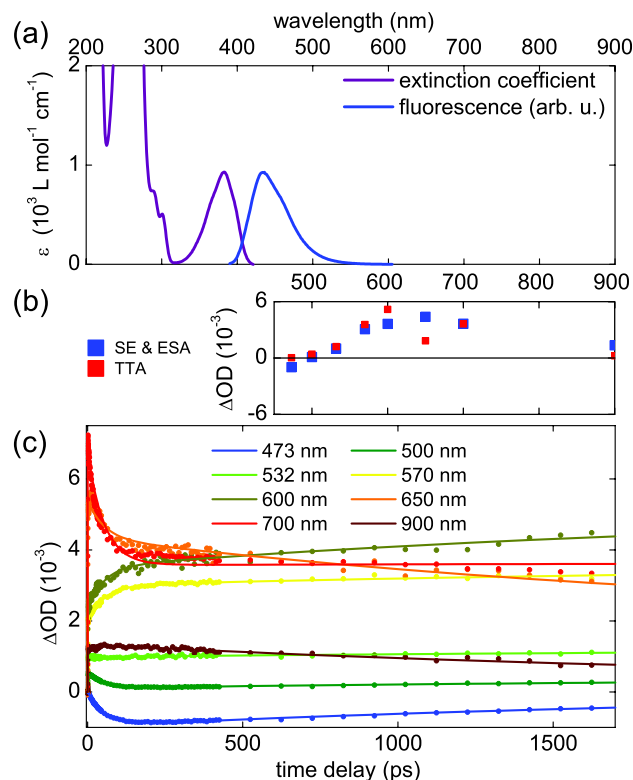


Fig. 2. (a) Molar decadic extinction coefficient (ϵ) and fluorescence spectrum of ITX in ethanol solution. (c) Time-dependent change of the OD, ΔOD (dots), after 387.5 nm excitation for different probe wavelengths as indicated. $\Delta OD < 0$ corresponds to increased probe transmittance upon optical pumping. The solid curves result from a global fit of a simple rate-equation model to these data. (b) Fit coefficients for the sum of SE and ESA (blue) and for TTA (red).

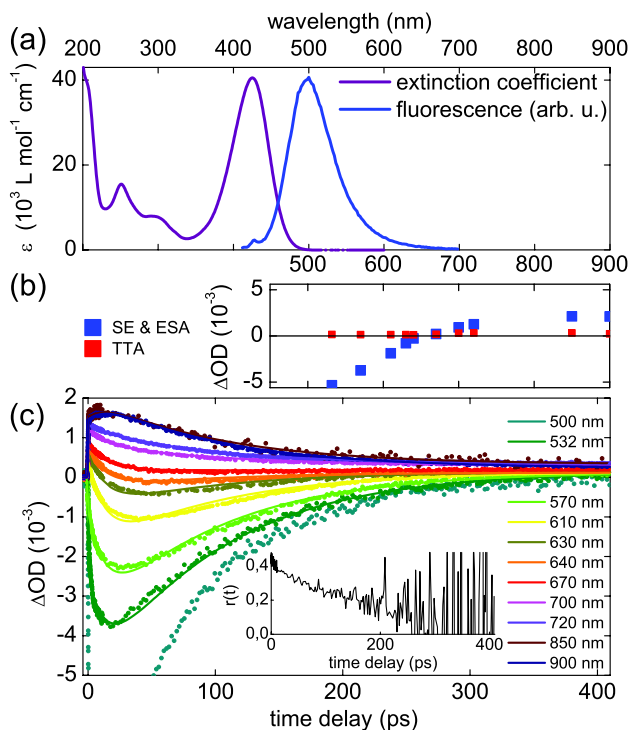


Fig. 3. Same as Fig. 2 but for the photoinitiator DETC in ethanol solution. Note the different time scale. Inset in (c): exemplary transient anisotropy $r(t)$ at 532 nm.

time constant τ_2 describes depopulation of the S_1 state via fluorescence and ISC. Both, SE and ESA decay with this time constant. In addition, triplet-triplet absorption (TTA) builds up and leads to a contribution with $\Delta OD > 0$. This leads to an expected signal versus time delay t of the form $\Delta OD(t) = Ae^{-t/\tau_1} + Be^{-t/\tau_2} + C(\tau_1 e^{-t/\tau_1} - \tau_2 e^{-t/\tau_2} + \tau_2 - \tau_1)$. Global fits of this model to the ITX data and DETC data are shown by the solid curves in Figs. 2(c) and 3(c). In case of DETC only probe wavelengths larger than 500 nm were used for fitting because of the proximity to the absorption band. For ITX, we find $\tau_1 = 48$ ps and $\tau_2 = 2.3$ ns, for DETC $\tau_1 = 13.8$ ps and $\tau_2 = 99$ ps. The corresponding amplitude coefficients for SE & ESA from $S_1 (= B)$ and TTA from $T_1 (= C(\tau_2 - \tau_1))$ are represented in Figs. 2(b) and 3(b). Furthermore, transient anisotropy data (e.g., inset in Fig. 3(c)) support the assignment of τ_2 . Thus, the overall agreement within the validity of the model is very good.

In conclusion, by employing femtosecond pump-probe spectroscopy, we have unambiguously found pronounced SE at 532 nm wavelength for the photoinitiator DETC. The gain decays on a 100 ps timescale, which is attractive for pulsed depletion in STED direct laser writing. In contrast, we find that ESA dominates for the case of ITX. Similar future pump-probe experiments on other novel photoinitiators might help in screening the numerous options for photoinitiators in STED photoresists for far-field optical lithography that is no longer limited by Abbe's diffraction barrier.

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