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Thresholds for nonlinear recording of fluorescent centers in chromone-doped polymer films

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Abstract Nonlinear recording of stable fluorescent microstructures in PMMA films doped with photosensitive compound 2-(furan-2-yl)-3-(thiophen-2-carbonyl)-chromen-4-one is investigated. Energy and power density thresholds for recording stable fluorescent marks and for film destruction and photobleaching of the fluorescent marks by laser pulses were measured in wide spectral (from 530 to 620 nm) and temporal (from 80 to 7 ns) ranges. The evidences of the sequential two-step excitation mechanism for the studied dye are presented. It was shown that picosecond pulse duration range is preferable for two-photon data recording. Quasi-Gaussian and donut shaped fluorescent marks with almost the same cross-section were recorded by femtosecond pulses with rather small difference in energies.

Keywords Chromone · Photosensitive organic compounds · Fluorescence · Two-photon excitation · Data recording · Archive memory

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1 Introduction

Rapid progress of information technology promotes significant development in creation of photosensitive media for 3D optical data carriers and data storage devices. Multilayer fluorescent discs are promising 3D optical data carriers (Barachevsky et al. 2011; Ayt et al. 2014; Krayushkin et al. 2009; Martynov et al. 2014). These disks allow data-reading from transparent information layers with distributed fluorescent centers in contrast to registration of reflected beam used nowadays in ordinary CD/DVD/BRD. Examples of constructions for multilayer fluorescent discs are demonstrated in patens (Gagarskiy et al. 2013b; Kiyko 2013). Such constructions provide both high data recording volume density and reliable parallel data reading.

A number of written layers is limited mostly by optical properties of writing beams, used material and focusing optics. For fluorescent discs the number of written layers may reach several hundred (Wang et al. 1997; Milster et al. 2001). Nonlinear recording of fluorescent centers provides its better localization and resolution. Nonlinear effects make it possible to write a single bit selectively anywhere within volume or layered structure by tightly focused laser beam or by intersecting of two laser beams (Hunter et al. 1990; Wang et al. 1997; Pudavar et al. 1999; Sivaraman et al. 2000; Milster et al. 2001, 2002; Dvornikov et al. 2009; Gu et al. 2013).

Photosensitive chromone-doped polymer film is a promising medium for development of WORM-type (write once read many) archive memory (Martynov et al. 2014; Ayt et al. 2014; Barachevsky et al. 2011; Krayushkin et al. 2009). In the present study, we used photosensitive polymer films with chromone 2-(furan-2-yl)-3-(thiophen-2-carbonyl)-

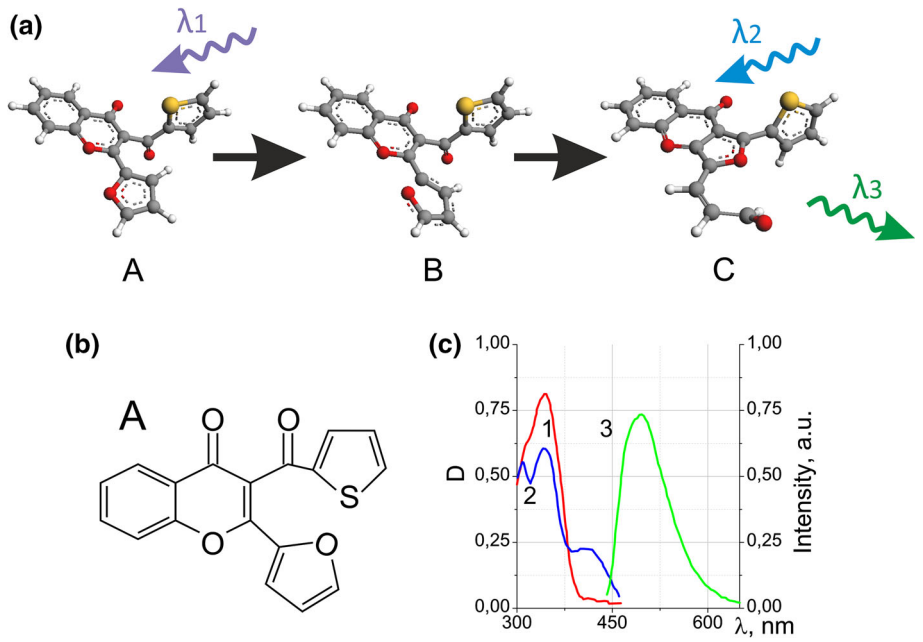

Fig. 1 **a** Scheme of photoisomerization process in chromone LHC480; **b** chemical structure of LHC480 compound; **c** absorption spectra of PMMA film with embedded LHC480 (5 wt%) in A form (1), C form (2), and luminescence spectrum of C form (3) excited at 405 nm

chromen-4-one compound [LHC480, marked as 10k in (Krayushkin et al. 2009)] (Fig. 1b). It should be noted that these chromone-based films absorb significantly in UV range and insignificantly in visible and IR range. LHC480 can be irreversibly converted from non-fluorescent form A to the stable fluorescent photoproduct C (Fig. 1a) via intermediate excited state B. Fluorescence excitation band of the C-form is shifted from absorption spectrum of A-form into visual spectrum (400–500 nm). It provides fluorescence excitation of the C-form without affecting A-form of the compound.

Data storage material is an essential element in the optical data storage system. Technical parameters such as threshold values of mark recording and damage fluxes, lifetime of the created marks and optical losses are particularly important. This work focuses on the study of multiphoton excitation in photosensitive media based on a preliminary selected chromone LHC480.

Energy and power density thresholds for recording stable fluorescent marks and for film destruction and photobleaching of the fluorescent marks by laser pulses were measured in wide spectral range from 530 to 620 nm and temporal range from 80 to 7 ns.

2 Experiment

In our two-photon fluorescent marks recording experiments we used several experimental facilities to determine threshold values of energy required for stable fluorescent bit patterns formation in wide spectral and temporal ranges.

As the samples we used thin (4–7 μm) PMMA films with embedded chromone compound coated on the glass substrates (170 μm). For preparing the films we used solution of PMMA and LHC480 in toluene. The films were made by spin-coating method. Weight concentration of LHC480 in dried films was 5%. Actual value of films thickness around a particular recorded mark was measured with confocal laser scanning microscope LSM-710 by detection of luminescence signal while scanning along Z-axis (Carl Zeiss GmbH 2008). This method allows detection of fluorescence signal with resolution of 0.6 μm in Z-direction.

As the sources of nanosecond and picosecond recording light pulses at different wavelengths we used diode-pumped neodymium lasers equipped with nonlinear optical devices such as second harmonic generators and Raman solid-state converters (Gagarskiy et al. 2013a, b). Laser system based on Ti–Sapphire master oscillator, sum frequency converters and optical parametric oscillators provided single femtosecond pulses with microjoule energy level and minimum pulse width of 60 fs at central wavelength tuned in the range of 530–620 nm (Fischer et al. 2011). In all cases temporal and spatial distribution of the focused beam was carefully measured to determine correlation between measured pulse energies and corresponding intensities on the tested sample. The focused beam size was more than 20 μm to provide direct measurements of the beam profiles at the target plane. Precision beam waist positioning within the samples was provided by scanning system with F-Theta lens or/and 3D program controlled actuators.

Recorded fluorescent marks were registered with confocal laser scanning microscope LSM-710 (LSM 710 and ConfoCor 3 2008). The system allowed defining profile of the recorded marks and its fluorescence spectrum with excitation at different wavelengths as 405, 488 or 514 nm.

We measured the energy and power density thresholds for recording of stable fluorescent marks (the mean values W_{ER} and W_{PR}), for film destruction and photobleaching of the

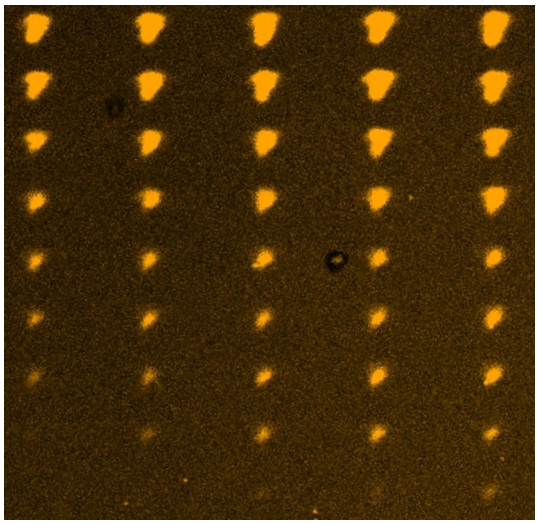

Fig. 2 Grid point pattern of fluorescent marks with variation of recording pulse energy

fluorescent marks (the mean values W_{ED} and W_{PD}). Threshold measurement was made by recording rectangular grid point pattern with variable energy (Fig. 2). Each point corresponds to single laser pulse with specified parameters. A point is considered to be recorded if signal-to-noise ratio (SNR) value for luminescent signal of corresponding area was 2 or higher. SNR was defined as a ratio of average luminescent signal at the point area to average background noise signal.

3 Results and discussion

We defined energy density value (W_{ED}) for laser induced thermal damage threshold (for nanosecond pulses) by the presence of observable film destruction. Power density threshold value (W_{PD}) for photosensitive compound bleaching was defined by appearance of fluorescence signal drop in the center of recorded mark profile. Typical pictures of recorded fluorescent marks obtained with scanning microscope are shown at Fig. 3. For used samples W_{ED} values in nanosecond range were only 20–30% higher than W_{ER}.

Thermal damage never occurred for the used femtosecond recording pulses. Recording power densities for 120 fs pulses exceeded 5 GW/cm^2. It was just a few percent less than W_{PD} value corresponding to partial photobleaching of fluorescent marks. That is a reason why donut-like mark profile caused by photobleaching in the center is observed when writing femtosecond pulse energy changes only within the range of 5%. For the pulses of hundreds picosecond duration and for energy up to 1.5 W_{ED} neither material damage nor irreversible photobleaching of fluorescent marks were observed.

Due to nonlinearity of recording process the radius of registered fluorescence pits measured as full width at half maximum (FWHM) was about 4–5 times smaller than the radius of writing laser beam for all used pulses durations. For the pulses of 120 fs measured power density threshold W_{PR} value increases in times in compare with pico- and nanosecond range at the same wavelength. For the pulses of 80 fs duration luminescent mark recording with one pulse was unsuccessful. The results for nonlinear recording for investigated films are shown in Tables 1 and 2.

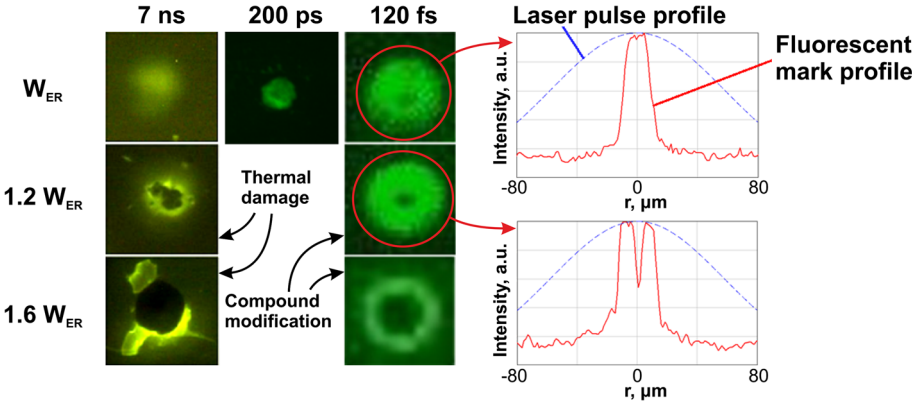

Fig. 3 Fluorescent marks recorded at different laser pulse parameters; profiles of marks and laser pulse

Table 1 Energy density W_{ER} and power density threshold W_{PR} values for stable fluorescent mark recording for chromone-doped PMMA films containing 5 wt% LHC480

Pulse duration	7 ns	2.5 ns	200 ps	120 fs	80 fs
Wavelength (nm)	532	532, 563, 598	563	620	530–620
W_{PR} (GW/cm^2)	0.4	1	1.5	5	⊗
W_{ER} (J/cm^2)	3	2.5	0.22	7×10^{-4}	⊗

Table 2 Energy density value W_{ED} for laser induced thermal damage threshold value and power density threshold value W_{PD} for photosensitive compound bleaching for chromone-doped PMMA films containing 5 wt% LHC480

Pulse duration	7 ns	2.5 ns	200 ps	120 fs	80 fs
Wavelength (nm)	532	532, 563, 598	563	620	530–620
W_{PD} (GW/cm^2)	Not reached	Not reached	Not reached	5.5	⊗
W_{ED} (J/cm^2)	3.4	3.2	Not reached	Not reached	⊗

The extreme increasing of recording threshold fluxes for the short femtosecond pulses evidences for the sequential two-step excitation mechanism similar to that observed in photochromic diarylethene compounds (Ward and Elles 2012, 2014). Those papers prove that barriers in the potential energy surface of the transient excited state exist in the diarylethenes. Time required for overcoming of those barriers is about a few picoseconds. This time defines the optimum duration of the recording pulse or temporal distance between sequential short pulses for providing maximum quantum efficiency of two-photon-induced photoisomerization (ring opening/closing process) (Fig. 4).

We suppose that a similar mechanism is relevant for the studied chromone despite much lower absorption at writing wavelength. With absorption of the first photon, an electron excitation to a transitional level occurs. That leads to corresponding changes of spatial distribution of molecular electron density. After that, geometry of nuclei positions starts to

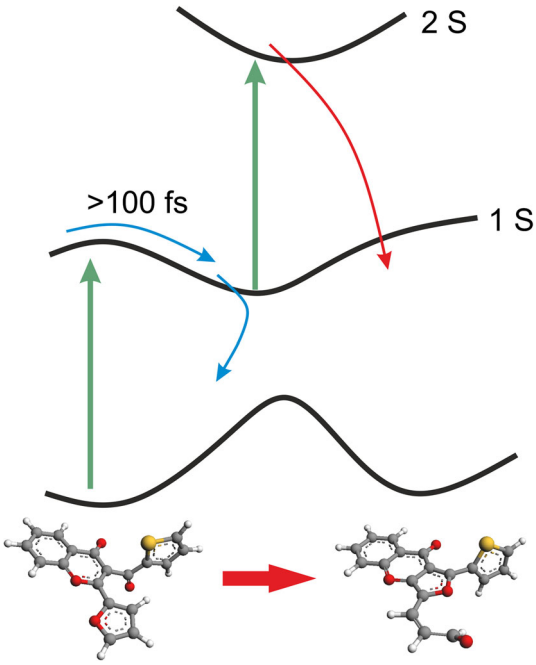

Fig. 4 Suggested diagram of sequential two-photon excitation of LHC480

change in accordance with distribution of molecular electron density for transient excitation state. If absorption time of the first photon and a corresponding reorganization of electron density is valued at 0.1 fs, then the reorganization of the nuclear configuration of molecule lasts more than 100 fs. Ratio of durations of these processes approximately complies with a mass ratio of electron and proton. The excited molecule must evolve on the excited potential energy surface to point which is more favorable for absorption of second photon and re-exciting of the molecule to a higher energy state with larger isomerization yield. To make a detailed study of the excited state dynamics and further optimization of the recording process, extra experiments using pump-probe, pump-repump-probe and pump-repump-fluorescence methods of ultrafast transient spectroscopy are being conducted.

4 Conclusion

Energy and power density thresholds for nonlinear stable fluorescent marks recording (W_{ER} and W_{PR}) in LHC480:PMMA films and for thermal destruction or photobleaching (W_{ED} and W_{PD}) of embedded compound were measured and compared in wide range of laser pulse durations and spectrum. It was shown that a picosecond pulse duration range is preferable for nonlinear data recording application. Measured W_{ER} and W_{PR} values for picosecond pulses are considerably lower both than thermal damage threshold of photosensitive material and compound bleaching threshold.

Due to nonlinearity of recording process the radius of recorded fluorescent pits is much smaller than the writing quasi-Gaussian laser beam radius. This allows the distance between pits to be less than the recording beam diameter and to increase information

recording density. The estimated recording density value is up to 1 Tbit/cm^3 for recording wavelengths of 600 nm.

Partial photobleaching of chromone compound under high intensity irradiation might be used for parameterized information recording (Gnatyuk et al. 2016) with ternary data storage system. Absence of fluorescence mark corresponds to logical zero, mark with quasi-Gaussian fluorescence distribution matches «1» and donut-like fluorescence distribution corresponds to «2».

For the pulses of 80 fs duration luminescent mark recording with one pulse was unsuccessful. The extreme increasing of recording threshold fluxes for the short femtosecond pulses indicates that the mechanism proceeds via a sequential two-step mechanism. Further optimization of temporal and spectral pulse parameters requires an additional investigation of two-photon excitation dynamics using fast pump-probe and pump-repump-probe technique.

References

Ayt, A., Barachevsky, V., Kobeleva, O., Valova, T., Gagarskiy, S., Kiyko, V., Sergeev, A., Veniaminov, A., Zakharov, V., Krayushkin, M.: Two-photon recording of stable luminescent centers in chromone-doped polymer films. IEEE (2014). doi:10.1109/LO.2014.6886252

Barachevsky, V., Krayushkin, M., Kyiko, V., Grebennikov, E.: Light-sensitive organic recording media for 3D optical memory. Phys. Status Solidi (c) **8**(9), 2841–2845 (2011). doi:10.1002/pssc.201084049

Carl Zeiss GmbH: LSM 710 and ConfoCor 3. Carl Zeiss MicroImaging GmbH (2008)

Dvornikov, A., Walker, E., Rentzepis, P.: Two-photon three-dimensional optical storage memory. J. Phys. Chem. A **113**(49), 13633–13644 (2009). doi:10.1021/jp905655z

Fischer, M.K., Gliserin, A., Laubereau, A., Iglev, H.: Ultrafast electron transfer processes studied by pump-repump-probe spectroscopy. J. Biophoton. **4**(3), 178–183 (2011). doi:10.1002/jbio.201000099

Gagarskiy, S.V., Gnatyuk, P.A., Sergeev, A.N., Khramov, V.Y.: Diode pumped solid-state lasers for volume 3-D marking of transparent dielectrics. J. Instrum. Eng. **56**(9), 12–17 (2013a) (in russian)

Gagarskiy, S.V., Kiyko, V.V., Kondratiyev, V.A., Sergeev, A.N., Khramov, V.Y., Yakobson, V.E.: Compression of diode-pumped microchip laser pulses by backward SRS-conversion. J. Instrum. Eng. **56**(9), 31–36 (2013b) (in russian)

Gnatyuk, V.A., Vlasenko, O.I., Levytskyi, S.N., Aoki, T., Mizeikis, V., Gagarsky, S.V., Zelenska, K.S., Gnatyuk, D.V.: Capabilities of laser-induced marks as information carriers created in different materials. J. Laser Micro Nanoeng. **11**(2), 164 (2016). doi:10.2961/jlmn.2016.02.0005

Gu, M., Cao, Y., Castelletto, S., Kouskousis, B., Li, X.: Super-resolving single nitrogen vacancy centers within single nanodiamonds using a localization microscope. Opt. Express **21**(15), 17639–17646 (2013). doi:10.1364/OE.21.017639

Hunter, S., Kiamilev, F., Esener, S., Parthenopoulos, D.A., Rentzepis, P.M.: Potentials of two-photon based 3-D optical memories for high performance computing. Appl. Opt. **29**(14), 2058–2066 (1990). doi:10.1364/AO.29.002058

Kiyko, V.V.: Device for recording and reading data on a multi-layer optical disc. USA Patent 8462603 (11 June 2013)

Krayushkin, M.M., Levchenko, K.S., Yarovenko, V.N., Zavarzin, I.V., Barachevsky, V.A., Puankov, Y.A., Valova, T.M., Kobeleva, O.I.: Synthesis and study of photosensitive chromone derivatives for recording media of archival three-dimensional optical memory. Arkivoc **9**, 269–283 (2009)

Martynov, I.Y., Barachevsky, V., Ayt, A., Kobeleva, O., Valova, T., Levchenko, K., Yarovenko, V., Krayushkin, M.: Fluorescence properties of light-sensitive chromones used in archival polymer recording media. Opt. Mater. **37**, 488–492 (2014). doi:10.1016/j.optmat.2014.07.011

Milster, T.D., Zhang, Y., Butz, J., Miller, T., Walker, E.: Volumetric Bit-Wise Memories. In: NASA Earth Science Technology Conference (2002)

Milster, T.D., Zhang, Y., Pinto, C., Walker, E.: A volumetric memory device based on photo-chromatic compounds. In: NASA Earth Science Technology Conference (2001)

Pudavar, H.E., Joshi, M.P., Prasad, P.N., Reinhardt, B.A.: High-density three-dimensional optical data storage in a stacked compact disk format with two-photon writing and single photon readout. Appl. Phys. Lett. **74**(9), 1338–1340 (1999). doi:10.1063/1.123543

Sivaraman, R., Clarson, S., Lee, B., Steckl, A., Reinhardt, B.: Photoluminescence studies and read/write process of a strong two-photon absorbing chromophore. Appl. Phys. Lett. **77**(3), 328–330 (2000). doi:10.1063/1.126966

Wang, M., Esener, S., McCormick, F., Çokgör, I., Dvornikov, A., Rentzepis, P.: Experimental characterization of a two-photon memory. Opt. Lett. **22**(8), 558–560 (1997). doi:10.1364/OL.22.000558

Ward, C.L., Elles, C.G.: Controlling the excited-state reaction dynamics of a photochromic molecular switch with sequential two-photon excitation. J. Phys. Chem. Lett. **3**(20), 2995–3000 (2012). doi:10.1021/jz301330z

Ward, C.L., Elles, C.G.: Cycloreversion dynamics of a photochromic molecular switch via one-photon and sequential two-photon excitation. J. Phys. Chem. A **118**(43), 10011–10019 (2014). doi:10.1021/jp5088948