「様式 3」

P-45

Laser-induced creation of long lifetime fluorescence centers in chromone-based materials for development of imaging formation techniques

[1] Organization

Project Leader: *Kateryna Zelenska*, M.Sci., Engineer (Taras Shevchenko National University of Kyiv, Ukraine).

Representative at RIE: *Toru Aoki*, Ph.D., Prof. (Research Institute of Electronics, Shizuoka University, Japan).

Participants:

Sergey Gagarsky, Ph.D., Senior Scientist (Saint-Petersburg National Research University of Information Technologies, Mechanics and Optics, Russia).

Volodymyr Gnatyuk, Ph.D., Assoc. Prof., Senior scientist (V.E. Lashkaryov Institute of Semiconductor Physics of the National Academy of Sciences of Ukraine, Ukraine).

[2] Progress of Scientific Activity

The CRP participants used communication facilities to discuss the collaborative project work and personally met, when Prof. Toru Aoki visited Ukraine for attending conferences in September and October 2015 and when Ukrainian project members visited RIE in September (The 14th Intern. Conf. on Global Research & Education: Inter-Academia-2015) and also in November 2015 – January 2016 thanks to support from CRP.

Apart from the investigations, described in the next section, the CRP team members organized the cooperative meetings in Ukraine and participated in the scientific forums in Ukraine and Japan to discuss the issues related to the project and establish collaboration and information exchange between Ukrainian and Japanese scientists and students. In particular, more than 10 students of Shizuoka University visited Ukrainian Universities in October 2015.

- Ms. *K. Zelenska* and Dr. *V. Gnatyuk* organized workshop “Education and Research in Shizuoka University” in Chernigiv National University of Technology, Ukraine (Sep. 2015) where Prof. *T. Aoki* made his talk and Ms. *K. Zelenska* reported about scientific and education exchange programs for Ukrainian researchers and students to visit Japan.
- Ms. *K. Zelenska* and Prof. *T. Aoki* organized the meting of Ukrainian and Japanese students at Chernigiv National University of Technology, Ukraine (Oct. 2015) to exchange the knowledge and information about education and research in Japanese and Ukrainian universities.
- Ms. *K. Zelenska* and Prof. *T. Aoki* organized the friendly meting of Ukrainian and Japanese students at the Ukraine-Japan Center in Oct. 2015 to discuss the issues of culture, education and scientific activity in Ukraine and Japan.
- Ms. *K. Zelenska* presented the project-related results at The 14th Intern. Conf. on Global Research & Education: Inter-Academia-2015) held at Shizuoka University (28-30 Sep. 2015, Hamamatsu, Japan).
- Ms. *K. Zelenska* and Prof. *T. Aoki* were members of the Organizing Committee and Dr. *V. Gnatyuk* was a member of the International Committee of The 16th Intern. Young Scientists Conf. “Optics & High Technology Material Science” SPO 2015 held at the Faculty of Physics of Taras Shevchenko National University of Kyiv (22-25 Oct. 2015, Kyiv, Ukraine).
- Ms. *K. Zelenska* presented the project-related results at the Monday Morning Forum at Research Institute of Electronics, Shizuoka University (30 Nov., 2015, Hamamatsu, Japan). This presentation was made owing to the business trip supported by CRP.

[3] Research Results

Short pulses of focused laser radiation have the unique capacity to change the properties of a small local area in the bulk of transparent objects because of non-ideal optical transparency of the employed material, its absorptive inhomogeneities (defects, inclusions, density fluctuations, etc.) and non-linear phenomena (multiphoton absorption, etc.) [1-7].

The project has been devoted to analysis and evaluation of laser-based techniques and technological approaches of formation of micromarks in the bulk of different materials transparent for a selected laser wavelength, which can serve as pixels for creation of images as well as information carriers for 2D and 3D digital optical recording. In particular, physical and photochemical processes occurring in the bulk of transparent light sensitive chromone-based materials under the action of focused short laser pulses were studied.

In conventional optical recording methods, crosstalk or interference of different recording components (marks) and layers often leads to reduced recording densities. It is possible, however, to improve the spatial resolution and thus the density of digital optical recording by using laser-induced marks which act as light emission centers under backlight illumination. The most promising materials for such a purpose are those in which a local change in the complex refractive index, structure or spectral-luminescent properties occurs in result of multi-photon absorption of ultrashort pulses of recording radiation [1-3, 5-7].

Organic molecules of chromones embedded in polymer matrix are promising media for optical data recording based on multiphoton absorption [3, 5-7]. These compounds can be irreversibly converted from the non-fluorescent form A to the stable fluorescent photoproduct C. (Figs. 1 and 2). The absorption spectrum of the photoproduct shows an additional excitation band in the visible range (400 nm), which was not observed in the state A. Thus, optical excitation in the spectral range between 400 and 500 nm leads to the stable fluorescence photoproduct C.

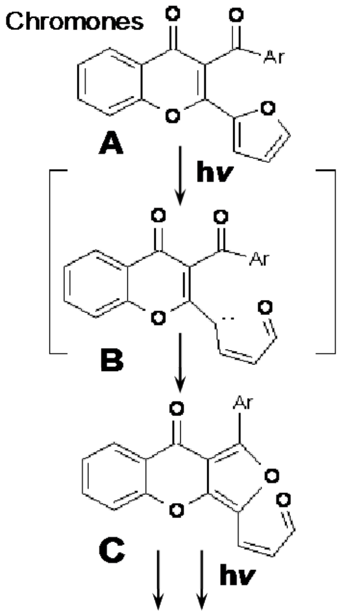

Fig. 1. Transformation of the chromone molecule structure because of two-photon absorption and it becomes fluorescent centers (light-emitting marks).

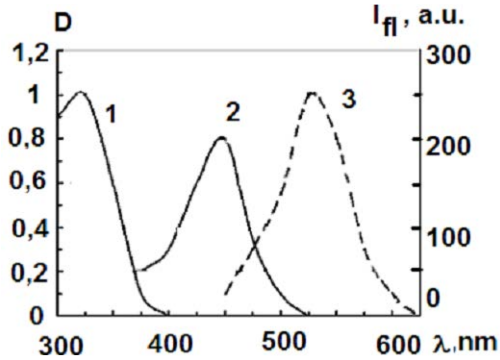

Fig. 2. Chromone compound: (1) – initial absorption spectrum in A state, (2) – fluorescence excitation spectrum in B state, (3) – fluorescence spectrum for C state.

Emitting centers can thus be obtained in thermally stable photosensitive organic chromone-based materials in selected layers by two-photon absorption of laser radiation with a wavelength that is not absorbed by the polymer matrix and chromone molecules [3, 5-7].

Separate organic molecules in the laser focal area change their structure because of two-photon absorption and they become fluorescent marks. The density of created marks depends on the energy and number of recording laser pulses. The distance between the neighboring emitting centers created in the polymer matrix with embedded chromone molecules by short laser pulses of a YAG:Nd laser (λ = 532 nm, τ = 0.8 ns) is about 5 μm and mark sizes are less than 2 μm (Fig. 3). The brighter marks were created by increasing the number of recording laser pulses. Fig. 4 shows marks obtained as result of two-photon absorption at different laser intensity: fluorescence centers (a) and damage points (b).

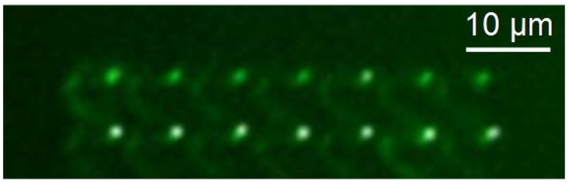

Fig. 3. Micrograph of laser-induced fluorescent marks formed in the volume of an organic chromone-based material by laser irradiation.

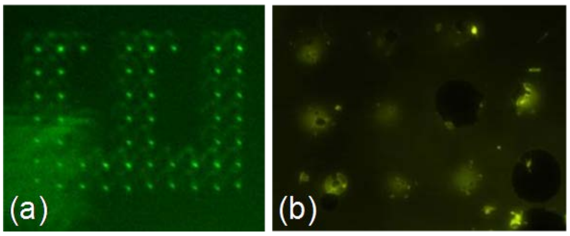

Fig. 4. Samples of fluorescent centers (a) and damage points (b) obtained under investigation of two-photon absorption in organic chromone-based materials.

The different number of laser pulses incident to the local area of a given mark leads to creation of different number of induced fluorescent centers and thus to different brightness level. Fluorescent marks with specific intensities can therefore be created by multi-shot laser irradiation and careful selection of the applied number of laser pulses. The resulting light emitting marks can consequently be read and classified in respect to their brightness by standard photodetection methods.

Since even a single molecule of chromone can serve as a fluorescent center and the waveguide layer thickness is limited by the reading radiation wavelength, the maximum recording density depends only on the recording laser beam caustic parameters.

Embedded information can in fact be read by injection of UV radiation into waveguide layers located between the photosensitive layers. In such a case the UV radiation partially penetrates into the adjacent layers with recorded marks and excites light emission from them due to fluorescence. Given that even a single chromone molecule can act as a fluorescent center and that the thickness of a waveguide layer can be as low as the reading radiation wavelength, the maximum recording density and spatial resolution depend only on the caustic of the recording laser beam and can closely approach the known theoretical limits.

The recording carried out by multi-photon excitation of organic molecules (photo-chromogenic chromones) and transition of them to a thermo-stable fluorescent state is much effective compared with another processes based on photoluminescence or refractive index change [3, 5-7].

Compounds consisting from chromones and diarylethenes are promising materials for data recording, optical switches and imaging. (Fig.5).

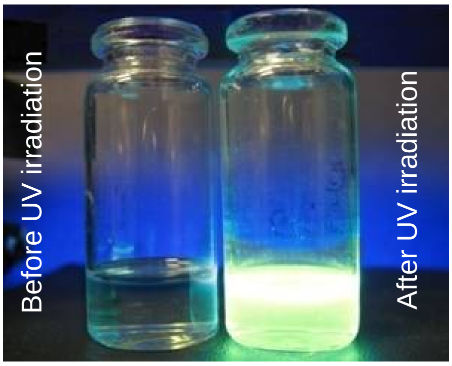

Fig. 5. Organic photosensitive chromone-based compound becomes light-emitting material after ultraviolet irradiation.

[4] Publications ***(published and submitted by the CRP participants during the project period 29.05.2015-06.03.2016)***

1. V.A. Gnatyuk, O.I. Vlasenko, S.N. Levytskyi, T. Aoki, V. Mizeikis, S.V. Gagarsky, K.S. Zelenska, D.V. Gnatyuk, Laser-induced creation of marks as information carriers for digital recording, *Program & Technical Digest, LAPM2015 - The 7th Intern. Congress on Laser Advanced Materials Processing*, 2015, Th2-LO-17, 185. (26-29 May 2015, Kitatyushu, Japan).
2. V.A. Gnatyuk, O.I. Vlasenko, S.N. Levytskyi, T. Aoki, V. Mizeikis, S.V. Gagarsky, K.S. Zelenska, D.V. Gnatyuk, Laser-induced creation of marks as information carriers for digital recording, *Proceed. of LAMP2015 - the 7th Intern. Congress on Laser Advanced Materials Processing*, (2015) 5 pages.
3. A. Ayt, V. Barachevsky, V. Kiyko, S. Gagarsky, A. Sergeev, A. Veniaminov, M. Krayushkin, H. Iglev, Two photon absorption and luminescent centers forming in photoswitchable media for multilayer optical disks, *Abstracts of The 10th Phenics Intern. Network Symp. "Photoswitchable Molecular Systems and Devices: From Synthesis to Applications"*, 2015, 47. (23-26 Nov. 2015, Cargese, France).
4. K.S. Zelenska, S.E. Zelensky, L.V. Poperenko, K. Kanev, V. Mizeikis, V.A. Gnatyuk, Thermal mechanisms of laser marking in transparent polymers with light-absorbing microparticles, *Optics & Laser Technology*, **76**, (2016) 96-100.
5. V.A. Gnatyuk, O.I. Vlasenko, S.N. Levytskyi, T. Aoki, V. Mizeikis, S.V. Gagarsky, K.S. Zelenska, D.V. Gnatyuk, Capabilities of laser-induced marks as information carriers created in different materials, *Journal of Laser Micro/Nanoengineering*, (2016), *in press*.
6. A, Ayt, V.A. Barachevsky, S.V. Gagarskiy, V.V. Kiyko, A.N. Sergeev, Y.Y. Sukhikh, A.V. Veniaminov, V.V. Zakharov, Fluorescent properties of chromone-class isomers converted by single- and multiphoton excitation, *The 17th Intern. Conf. "Laser Optics 2016" (LO'2016)*, 2016, 1 page. (27 June - 1 July 2016, Saint Petersburg, Russia), *submitted*.
7. S.V. Gagarsky, A. Ayt, V.A. Barachevsky, A. Duensing, H. Iglev, V.V. Kiyko, M.M. Krayushkin, A.N Sergeev, V.V. Zakharov, Thresholds for two-photon recording of fluorescent centers in chromone-doped polymer films, *Intern. Symp. "Fundamentals of Laser Assisted Micro– and Nanotechnologies" (FLAMN-16)*, 2016, 1 page. (27 June - 1 July 2016, Saint Petersburg, Russia), *submitted*.

Traveling Report

Name:	Kateryna Zelenska
Affiliation and address:	Taras Shevchenko National University of Kyiv, 64/13 Volodymyrska Street, Kyiv, 01601, Ukraine
Period of time:	15 November 2015 – 13 January 2016
Destination:	Research Institute of Electronics, Shizuoka University
Purpose:	Study of laser technological approaches suitable for volumetric optical recording and image formation by creation of micromarks in the bulk of different materials, particularly in transparent light sensitive chromone-based materials under action of focused short laser pulses. Participation in scientific meetings at Research Institute of Electronics, Shizuoka University during the period of stay.
Name of receiver:	Prof. Toru Aoki