Two-Photon Recording of Stable Luminescent Centers in Chromone-Doped Polymer Films

A. Ayk, V.A. Barachevsky, O.I. Kobeleva, T.M. Valova
Photochemistry Center of RAS
Moscow, Russia

S.V. Gagarsky, V.V. Kiyko, A.N. Sergeev, A.V. Veniaminov, V.V. Zakharov
NRU ITMO
St.Petersburg, Russia

M. Kravushkin
N.D. Zelinsky Institute of Organic Chemistry
Moscow, Russia

Hristo Iglev
Physik-Department
Technical University of Munich
Garching, Germany

Abstract — The study defines threshold values of energy density required for two-photon writing of stable fluorescent bit patterns within polymer layers containing chromones class chemical compounds by visual laser pulses in range of pulse widths from nanoseconds to femtoseconds. Photo-regrouping of non-luminescent chromones to fluorescent products is shown as the result of true type two-photon absorption (TPA) and stepwise TPA as well. In the latter case writing beam fluence can be reduced due to increase of the effective TPA coefficient, but laser-induced thermal damage of matrix becomes more probable too.

Keywords — chromone; fluorescence; two-photon absorption; information recording; laser induced damage

Multilayer optical disks based on photosensitive registering media with two-photon writing - fluorescence reading method (TPWFLR) are now considered as promising media for three-dimensional optical data storage with enhanced capacity. The principle difference of fluorescent optical disks is reading of fluorescent marks created in working layer as opposed to reflected beam used in modern optical CD/DVD/BRD. In addition, TPWFLR method seems to be promising and easy-to-implement technique for products and construction parts marking. Organic molecules of chromones class stand out sharply among of known photosensitive compounds. These molecules demonstrate irreversible conversion of non-fluorescent form A to the stable fluorescent photoproduct B under UV action. B-product fluorescence excitation bands lies in near-UV and visual spectrum (300-500 nm).

This paper focuses on the study of features of laser TPA processes with chromones of different types and on the determination of pulse energy required for information pits writing in dependence of pulse duration and wavelength.

Pulses of $10^{13}$ – $10^{15}$ s were used to determine the threshold values of energy and power density required for stable photosensitive bit patterns creation. Femtosecond pulses tuned in the range of 560-620 nm were obtained with Ti:sapphire - OPO laser system. Diode pumped Nd:YVO laser equipped with second harmonic converter was used as nanosecond pulses source. Due to squared dependence of TPA coefficients on intensity the ratio of FWHM beam transverse dimension and luminescent pits near the recording threshold was of 5:1. Threshold value of writing pulse power density ($W_{WR}$) implies light density sufficient for resolved information pits transversely illuminated by additional light source. As the samples we used thin amorphous polymer films with several types of chromones as KSR15, LHC480, LHC886: PMMA. After writing the fluorescent images were analyzed with confocal scanning microscope LSM710 (Zeiss MicroImaging GmbH) based on upright microscope AXIO Observer.Z1. Fluorescence of the created pits was exited with CW diode laser ($\lambda=405$ nm) or argon laser ($\lambda=488$ nm) with mW output. Laser induced thermal damage threshold of the investigated materials ($W_{LID}$) or non-luminescent state molecule transition was defined by the presence of a drop at the middle of fluorescent pit profile.

It was measured to be that threshold values of $W_{WR}$ is of 3.6 J/cm² in the 5% KSR15 type chromon - doped PMMA for 5 ns pulses at 532 nm. The value corresponds to peak intensity of 0.45 GW/cm². $W_{WR}$ value is of 690 $\mu$J/cm² for 160 fs pulses at 600 nm wavelength and relevant intensities ~ 5 GW/cm². It was found that difference of $W_{WR}$ and $W_{LID}$ values is slightly less for nanosecond pulses but it is no more than 20% both for the long and short pulses. This point is explained by more effective stepwise TPA in the case of nanosecond pulses use.

Based on the results of the study the estimated values for energy required for two-photon record of fluorescent images with help of most favorable picosecond pulses ($\tau=10^{-11}$ s) of yellow-red spectral range are of 0.2-0.3 nJ if the writing beam is focused into the spot size of 2-3 wavelengths. In this case luminescent pit size can be even less than writing wavelength. For the pulse repetition rates of 100 MHz it is required to use sources of picosecond pulses generating in visual range with average power of ~ 20 mW. This value could be decreased if optimizing parameters of focused writing beam and polymer film composition including nano structuring. Thus the studies show an actual realization of two-photon method of information writing in chromon doped polymer films with the visible pulses in wide range of pulses duration. Available recording density is of 1 Tbit/cm² and characterized by storage time of recorded information at room temperature over dozens years. The parameters are perspective for industrial production of TPWFLR optical cartridges based on chromone-doped polymer films and theirs application in up-to-date information recording and storage systems.