



SIXTH INTERNATIONAL
WORKSHOP

**“RELAXED, NONLINEAR
AND ACOUSTIC OPTICAL
PROCESSES AND
MATERIALS”**

RNAOPM'2012

PROCEEDINGS

Lutsk – Shatsk Lakes, May 25–29, 2012

To 50-th anniversary of Nonlinear Optics
and
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*До 50-річчя нелінійної оптики
та
20-річчя релаксаційної оптики*

МАТЕРІАЛИ
VI МІЖНАРОДНОЇ НАУКОВОЇ КОНФЕРЕНЦІЇ

LUTSK-2012

ON THE GENERALIZED STRETCHED EXPONENTIAL FUNCTIONAL PARAMETERIZATION OF PHOTODARKENING KINETICS IN AMORPHOUS CHALCOGENIDES WITHIN PASS FORMALISM

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In this paper, the kinetics of *in-situ* photodarkening was carefully described at the example of As₆₀Se₄₀ thin films to justify its revealing under a wide variety of known experimental-measuring conditions. We have studied the films of different thicknesses and thermal pre-history pumping with the same absorbed light beam having different penetration depths. The principal conclusion of this research is that the *in-situ* photodarkening itself is governed by a single exponential rule, but in dependence on penetration depths of pumping light this behaviour attains a stretched character. The smaller penetration depth in respect to the film thickness, the more dispersive behaviour is revealed in the photodarkening kinetics parameterized with stretched exponential law.

Key words: *in-situ* photodarkening, penetration depth, relaxation kinetics, photon-assisted site switching, single exponential function, stretched exponential relaxation.

Amorphous chalcogenides like binary arsenoselenides As-Se are known to be unique disordered materials possessing extremely high sensitivity to external factors. As an example, the photo-induced optical effects, extensively studied since the early 1970-s [1,2], have been put in a ground for chalcogenide-based sensors, optical memory and switching devices, information storage systems, etc. These photoinduced effects clearly demonstrate two principally different components in chalcogenide films, the transient occurring under *in-situ* photoexposure and metastable or permanent ones leaving for a long time in the illuminated films after photoexposure stopping (*ex-situ* photodarkening) [3,4]. It is suggested that principal under-illumination *in-situ* photodarkening is rather non-dispersive in nature, being governed by single exponential relaxation kinetics corresponding to elementary activation processes initiated by over-band-gap transitions, provided the absorbed pumping light penetrates film body sufficiently deeply through a whole thickness [5]. In contrast, the just-relaxing transient part of photodarkening (a so-called dynamic component) forming long-lived metastable changes is more dispersive, being dependent probably on the basic relaxation interaction in the system, in particular, on the relation between short- and long-range molecular relaxation-driven forces [6,7]. However, under short penetration depths of pumping light, the *in-situ* photodarkening attains a more dispersive character in the film, tending the overall kinetics towards known stretched exponential law in the form of $\sim \exp(-t/\tau)^\beta$ with non-exponentiality index (dispersion parameter) $0 < \beta < 1$ and effective time constant τ [6,7].

The studied As₆₀Se₄₀ films of different thicknesses ($d=0.54 \div 4.07 \mu\text{m}$) were prepared by flash thermal evaporation in a vacuum onto glass substrates held at 100° C [8]. To initiate photostructural transformation in the studied films, the He-Ne laser ($\lambda=633 \text{ nm}$, $W=10 \text{ mW}$) was used. Optical transmission spectra of films in 0.3÷0.8 μm spectral range were recorded with UV/VIS Specord spectrophotometer (CARLZEISS Jena).

The kinetics of *in-situ* photodarkening was determined by relative transmission decrease T/T_0 (T_0 – initial optical transmission at $\lambda=633 \text{ nm}$ before illumination) and further fitted by stretched exponential relaxation function in the form of

$$T/T_0 = ae^{(-t/\tau)^\beta} + b, \quad (1)$$

where a reflects absolute magnitude of photodarkening, τ and β are effective response time and dispersion parameter, respectively.

All numerical comparisons for *in-situ* photodarkening behavior were performed in respect to the penetration depth of pumping light for as-prepared films before illumination

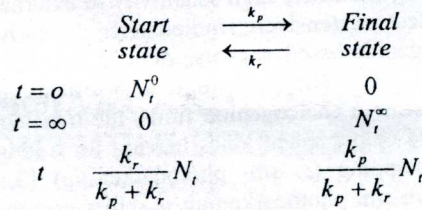
$$d^* = 1/\alpha, \quad (2)$$

where α is initial optical absorption coefficient of film, which, in turn, was estimated from known reflection coefficient R accordingly to the expression below:

$$\alpha = -\frac{1}{d} \ln \frac{(1-R)^2}{T}. \quad (3)$$

We accepted, in full agreement with [1], that thin film reflectance R was invariant during illumination, at least, in the range of fundamental optical absorption edge, where photodarkening effect was probed.

The kinetics peculiarities of photodarkening in thin chalcogenide films are known to be satisfactorily described in terms of photon-assisted site switching (PASS) facilitating percolative growth of atomic clusters at ground state [3]. Within this formalism, the final photodarkened sites (independently on their origin) having higher energy, are supposed to be formed from original (start) sites, giving a dynamic intersite balance owing to straightforward (production) and backward (relaxation) reactions. So overall set of photoinduced defect production-relaxation processes along with initial conditions can be conveniently presented via a scheme below:



where N_i^0 is initial concentration of atomic sites available for relaxation; k_p and k_r are probabilities of precursor trapping and detrapping in final state, respectively.

A necessary condition for experimental observation of photoinduced changes in optical properties of thin films corresponds to $k_p > k_r$. The general differential equation, which governs population of structural defects responsible for photodarkening N in an arbitrary time moment t can be presented as:

$$\frac{dN}{dt} = k_p(N_i - N) - k_r N. \quad (4)$$

By suggesting that overall concentration of atomic sites evolved in photoinduced structural transformations does not change during illumination, being nearly constant $N_i = \text{const} = N_i^0$, the above equation can be transformed to:

$$\frac{dN}{dt} = k_p N_i^0 - k_p N - k_r N = k_p N_i^0 - N(k_p + k_r). \quad (5)$$

This eq. (6) has simple solution, which can be presented in a single exponential form:

$$N = a \left(1 - e^{(-t/\tau)} \right), \quad (6)$$

where $a = \frac{k_p}{k_p + k_r} N_i^0$ is normalized magnitude of photoexcited sites.

However, in case of dispersive nature of underlying photostructural transformations, the following change of variables should be undertaken in eq. (6) [9]:

$$(kt) \rightarrow (kt)^\beta = \xi \quad (8)$$

with non-dispersivity index $0 \leq \beta \leq 1$ and $k = k_p + k_r$.

This allows to introduce a new rate equation relative to this variable ξ :

$$\frac{dN}{d\xi} = \frac{k_p}{k} N_i^0 - \frac{k_p + k_r}{k} N = \frac{k_p}{k} N_i^0 - N = \frac{k_p N_i^0 - kN}{k} \quad (9)$$

with solution giving growing-like kinetics in a stretched exponential form:

$$N = a \left(1 - e^{(-\xi)^\beta} \right). \quad (10)$$

This solution can be easily transformed to eq. (1), provided an opposite decaying behaviour is responsible for photoexcited sites growth in the film.

In order to justify conclusions on a decisive role of penetration depth for *in-situ* photodarkening kinetics, the $As_{60}Se_{40}$ films of different thicknesses were selected (Fig. 1).

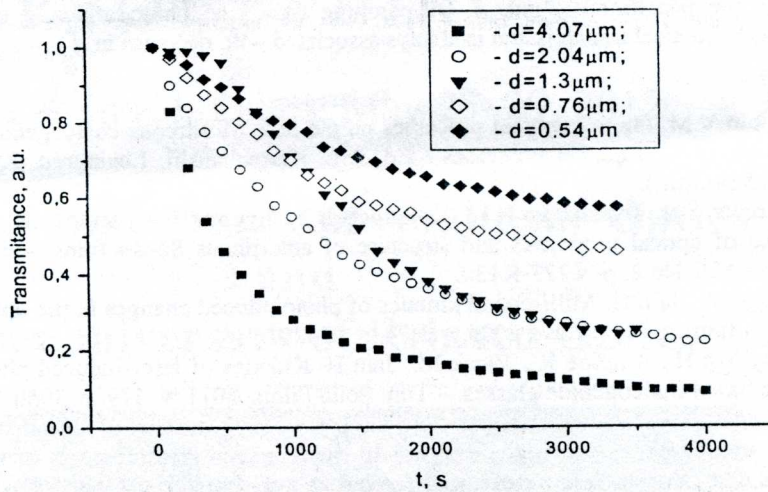


Fig. 1. Kinetics dependencies of normalized optical transmittance for He-Ne laser beam in $As_{60}Se_{40}$ films of different thicknesses.

With a purpose of adequate mathematical description of observed *in-situ* photodarkening kinetics, the numerical values of fitting parameters in eq. (1) (thickness, relation between penetration depth and thickness, non-exponentiality index β and normalized photodarkening magnitude A) were calculated in such a way to minimize mean-square deviations of experimentally measured points from stretched exponential law (1). The results of modelling are given in Table 1. It is obvious, when film thickness d is smaller than penetration depth of light beam d^* , the dispersion parameter $\beta=1$, indicating that the *in-situ* photodarkening dynamics can be presented by an exponential function. Under the condition $d > d^*$, the above dynamic response occurs dispersive in a nature and hence it can be presented by stretched exponential relaxation function (1). The dispersive photodarkening kinetics

obeying stretched exponential rule is observed in relatively thicker films, while in thinner films this kinetics corresponds to single exponential function, justifying that photostructural transformations themselves are non-dispersive in a nature.

Table 1. Fitting parameters τ and β in eq. (1) for photoexposed $As_{60}Se_{40}$ films of different thicknesses

$d, \mu m$	d^*/d	β	A
4.07	0.91	0.27	0.99
2.04	1.81	0.97	0.82
1.3	2.85	0.99	0.76
0.76	4.87	1.00	0.66
0.54	6.85	1.00	0.51

As known, the penetration depth d^* is a material-related parameter for a given pump light (of the same characteristics – energy/wavelength, power density, exposure, etc.). It means that d^* is defined only by material under exposure (molecular and chemical composition, structural state, etc.). So the despersivity of photodarkening can be effectively guided with changing in material thickness d (due to interrelation between d and d^*). This process is limited by film thickness (thickness-limited), since during illumination the film material undergo significant modification because of photostructural transformations, which change the penetration depth d^* of pumping light (the photodarkening or photoinduced decrease in optical transmission is always associated with decrease in d^*).

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