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On the governed kinetics describing *in-situ* photodarkening in thin As-Se films

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The kinetics describing in-situ photodarkening in amorphous $As_{100-x}Se_x$ thin films for different compositions as well as for various thicknesses were studied. It was shown this kinetics strongly depended on penetration depth parameter (the inverse value of the absorption coefficient): in the case that films thickness is greater than penetration depth, the photodarkening kinetics can be described by stretched exponential function. In contrast, if film thickness is less than penetration depth, the stretched exponential relaxation kinetics tents towards simple exponential one.

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1. Introduction

Amorphous chalcogenides like binary arsenoselenides are known to be unique disordered materials possessing extremely high sensitivity to external factors [1-3]. As an example, the photo-induced optical effects typically revealed themselves in photodarkening (e.g. long-wave shift of fundamental optical absorption edge), extensively studied since the early 1970-s [1], have been put in a ground for chalcogenide-based sensors, optical memory and switching devices, information storage systems, etc. [3].

These photoinduced effects clearly demonstrate two principally different components in chalcogenide films, the transient changes 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) [4,5]. 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 [6,7]. 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 [8,9]. 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 low in the form of $\sim exp(-t/\tau)^{\beta}$ with non-exponentionality index (dispersion parameter) $0<\beta<1$ and effective time constant τ [4,6,7].

So with changing in optical absorbance in respect to film composition and/or thickness, as well as testing conditions at which the photodarkening is probed (first of all, the ambient temperature), respectively to the penetration depth of pumping light used, the governed kinetics describing overall *in-situ* photodarkening can be significantly modified from single exponential (β=1) to non-exponential one ($0<\beta<1$) [6]. The question on a strict measure where exponential $\sim exp(-t/\tau)$ low becomes governed in the photodarkening kinetics remains open, despite numerous attempts to do this for different chalcogenide films. Thus, in [6], the transition to single exponential photodarkening kinetics was observed in thermally evaporated As_2Se_3 films having 200 nm thicknesses, which is nearly triple less as estimated value of penetration depth for pumping He-Ne laser beam in these films. At the same time, the governed kinetics for *in-situ* photodarkening remains stretched exponential with β=0.87 in thin As_2S_3 films of 1 μm thickness [4], which is more than 2.5 times less than estimated penetration depth for pumping light. There was also no transition to single exponential kinetics in amorphous $As_{45}Se_{55}$ films of 1 μm thickness pumped by λ=532 nm diode solid state laser in spite of liquid He measuring temperature in [10] (as it follows from experimental data presented in [10], the β value dropped down from nearly 0.45 at room temperature to 0.85 at 4.2 K, but did not attain β=1). The latter result seems quite reasonable as accept that the penetration depth of pumping light was extremely low in this case (the optical absorption edge of studied $As_{45}Se_{55}$ films was far beyond the pumping laser wavelength of λ=532 nm). So we expect the transition to single exponential photodarkening kinetics will be observable only in very thin $As_{45}Se_{55}$ films.

In this view, the conclusion that stretched exponential relaxation low always gives the better agreement with experimental data on photodarkening in As-S/Se films (independently on their thickness) seems, at least, discussible, even for optical measurements performed at low temperatures such as 78 or 4.2 K, when the penetration depth of pumping light is significantly increased because of temperature dependence of optical band gap [11,12]. An opposite decision on simple exponential kinetics (not stretched exponential one) for *in-situ* photodarkening in amorphous $As_2(S/Se)_3$ films illuminated by near over-gap photons was put forward later as an exemplification of top controversy in this field [13,14]. And finally, in [15], a strict correlation between stretching parameter β and penetration depth was revealed for photodarkening kinetics in $Ge_5As_{41}S_{15}Se_{39}$ thin films exposed by photons of different penetration ability. With illumination by over-gap photons effectively absorbed by this film, more photostructural processes proceed simultaneously giving a stretched exponential kinetics, while low-absorbed light causes ideal single exponential photodarkening kinetics.

Similar kinetics-changing effects can be affected also by intensity of pumping light. As it follows from [5], under He-Ne laser beam of increased intensity (from 40 to 160 mW/cm^2), the time evolution of optical transmission of $As_{50}Se_{50}$ thin films attains an accelerated character practically without any significant changes in the saturation state.

Such behavior is known [16] to be associated with enhanced dispersivity leading to the decrease in the stretching parameter β (most probably, this is due to variety of activated processes accompanying intensity-increased photoexposure). At lower light intensity (20 mW/cm^2 in [5]), the magnitude of photoinduced saturation is partly depressed, being somewhat less, but stretched exponential character of photodarkening kinetics is further obvious. High-intensity photoexcited states can spontaneously relax towards low-intensity state in the dark after photoexposure turn-off, this self-bleaching kinetics being also dispersive in a nature with time duration extending a few months [14].

In this paper, we shall try to justify the realistic governed kinetics for *in-situ* photodarkening in amorphous arsenoselenide films pumping with the same light beam having different penetration depth in each sample. With this in mind, we shall deal in our research with thickness (1), technological (2) and compositional (3) changing tendencies in the photodarkening kinetics by testing films of different thicknesses (from 0.54 to 4.07 μm), pre-history (virgin and annealed) and chemical composition ($As_{40}Se_{60}$, $As_{50}Se_{50}$ and $As_{60}Se_{40}$).

2. Experimental

$As_{100-x}Se_x$ films of different thicknesses (d=0.54÷4.07 μm) were prepared by flash thermal evaporation in a vacuum onto glass substrates held at 100 ^{o}C. One part of films was additionally annealed at T=120 ^{o}C during 1 hour to produce small darkening in respect to un-annealed films.

To initiate photostructural transformation in the studied films, we used a He-Ne laser (λ=633 nm, W=10 mW) operated in CW irradiation mode. Experimental set-up shown in Fig. 1 allowed simultaneous photodarkening activation and *in-situ* optical transmission measurements at the same wavelength of λ=633 nm [17].

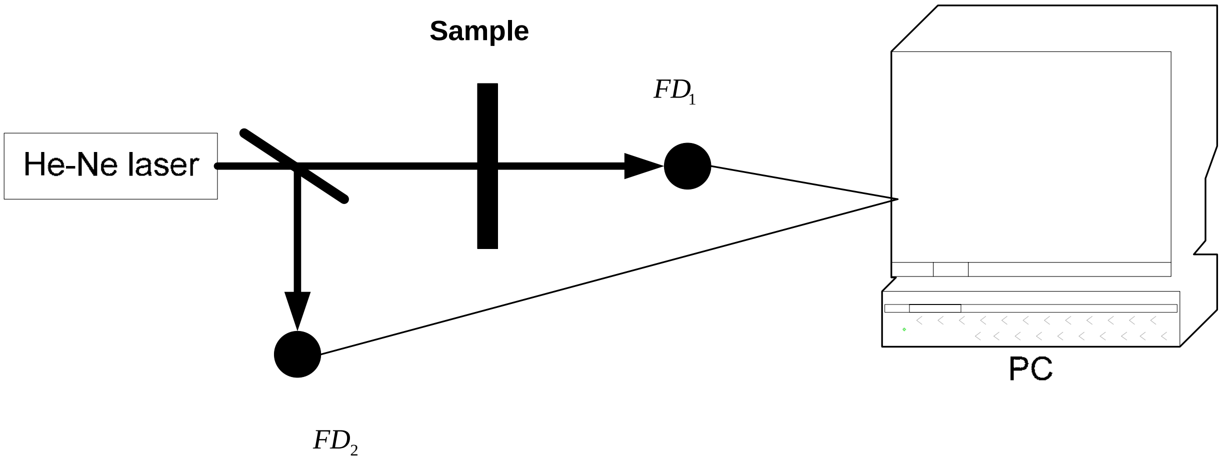


Fig. 1. Experimental set-up for in-situ photodarkening measurements.

The laser beam was divided by splitter on two ones, controlling film transmittance with Si photodetector FD_1 and time stability of laser beam intensity with other detector FD_2. Thus, the film transmittance was currently controlled during photoexposure using a registration module based on digital build-in PC-card PCI-1713 for data acquisition. Special software was elaborated for automatic measurements. So in our experiments, the same laser beam was used to perform dual *in-situ* function, the source of absorbed photons producing a measurable photodarkening effect and probing tool to measure the magnitude of this effect, like as in [18]. Optical transmission spectra of films in 0.3÷0.8 μm spectral range were recorded with UV/VIS Specord spectrophotometer (CARLZEISS Jena). Typical view of optical transmission spectra for amorphous $As_{40}Se_{60}$ films of 3.08 μm thickness in as-deposited, light exposured and thermally treated states are shown in Fig. 2.

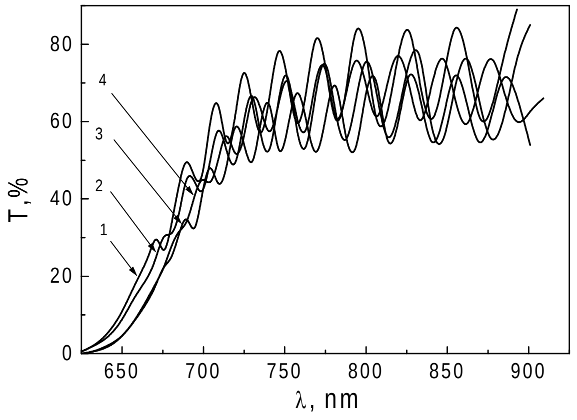


Fig. 2. Optical transmission spectra of $As_{40}Se_{60}$ films (d = 3.08 μm) in different states: 1 – as-deposited; 2 – as-deposited and thermally-annealed; 3 – as-deposited and light-exposured; 4 – thermally-annealed and light-exposured.

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

$$T/T_0 = ae^{\left(-t/\tau\right)^{\beta}} + b \tag{1}$$

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

It should be noted that A parameter calculated as ratio of coefficients from eq. (1)

$$A = \frac{a}{a+b} \tag{2}$$

can be accepted as a normalized measure of photodarkening magnitude.

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

$$d^* = 1/\alpha\ , \tag{3}$$

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

$$\alpha = -\frac{1}{d}\ln\frac{(1-R)^2}{T}\ . \tag{4}$$

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.

3. Results and discussion

The kinetics peculiarities of photodarkening in thin chalcogenide films can be satisfactorily described in terms of photon-assisted site switching (PASS) facilitating percolative growth of atomic clusters at ground state [4].

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 the overall set of photoinduced defect production-relaxation processes along with initial conditions can be conveniently presented via a scheme:

$$\begin{array}{cccc}
 & \textit{Start state} & \underset{k_r}{\overset{k_p}{\rightleftarrows}} & \textit{Final state} \\
t = o & N_t^0 & & 0 \\
t = \infty & 0 & & N_t^\infty \\
t & \dfrac{k_r}{k_p + k_r}N_t & & \dfrac{k_p}{k_p + k_r}N_t
\end{array},$$

where N_t^o 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:

$$\frac{dN}{dt} = k_p\left(N_t - N\right) - k_r N\ . \tag{5}$$

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

$$\frac{dN}{dt} = k_p N_t^{\,0} - N\left(k_p + k_r\right). \tag{6}$$

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

$$N = a\left(1 - e^{\left(-t/\tau\right)}\right), \tag{7}$$

where $a = \dfrac{k_p}{k_p + k_r} N_t^{0}$ corresponds to the maximum 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) [19]:

$$(kt) \to (kt)^{\beta} = \xi \tag{8}$$

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

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

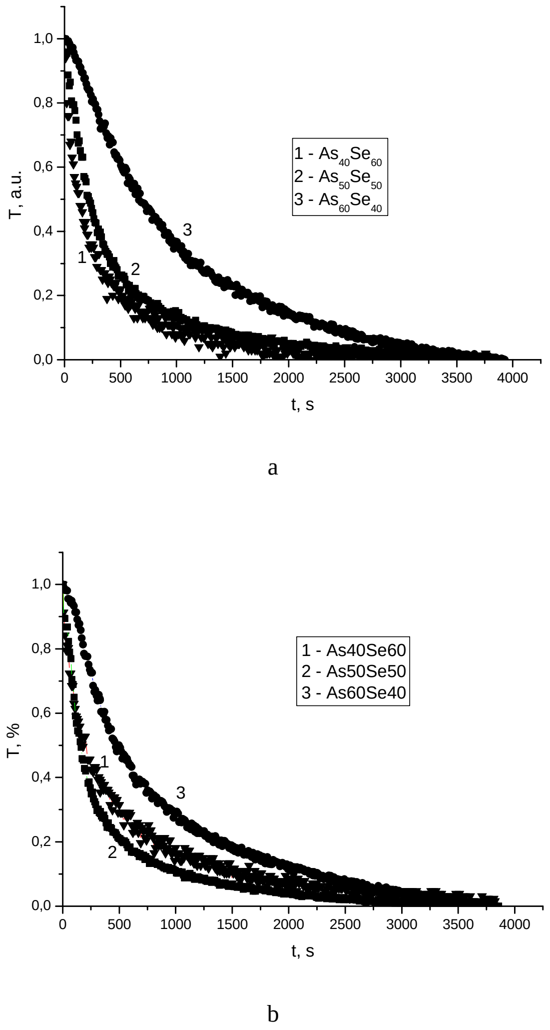
$$\frac{dN}{d\xi} = \frac{k_p N_t^{o} - kN}{k} \tag{9}$$

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

$$N = a\left(1 - e^{\left(-t/\tau\right)^{\beta}}\right). \tag{10}$$

This solution can be easily transformed to eq. (1), provided an opposite decaying behaviour is responsible for photoexcited sites growth in the film. The same conclusion on transition to stretched exponential photodarkening kinetics can be numerically justified for thicker films composed of a few elementary thin layers, each of them having non-dispersive single-exponential response [7]. The non-dispersivity in this case appears as a result of inverse proportionality between response times and pumping light intensity obeying simple Beer–Lambert–Bouguer law related the absorption of light to the properties of the material through which the light is travelling.

The kinetics dependencies of normalized optical transmittance for He-Ne laser beam for studied thin films of different chemical compositions ($As_{40}Se_{60}$, $As_{50}Se_{50}$ and $As_{60}Se_{40}$) and thermal pre-history (un-annealed and annealed), but nearly the same thicknesses (1.3 μm) are shown in absolute and normalized determinations in Fig. 3.



a

b

Fig. 3. Time evolution of normalized optical transmittancefor He-Ne laser beam in un-annealed (a) and annealed (b)$As_{40}Se_{60}$, $As_{50}Se_{50}$, $As_{60}Se_{40}$ *thin films.*

With a purpose of adequate mathematical simulation of the observed *in-situ* photodarkening kinetics, the numerical values of fitting parameters in eq. (1), e.g. effective time constant τ, non-exponentionality 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 low (1).

The results of modelling are given in Table 1.

Table 1. Fitting parameters in eq. (1) for studied $As_{40}Se_{60}$, $As_{50}Se_{50}$ and $As_{60}Se_{40}$ thin films.

Thin film	τ (s)	β	A
$As_{40}Se_{60}$ un-annealed	1000	0.64	0.76
$As_{40}Se_{60}$ annealed	400	0.54	0.61
$As_{50}Se_{50}$ un-annealed	300	0.74	0.83
$As_{50}Se_{50}$ annealed	246	0.66	0.87
$As_{60}Se_{40}$ un-annealed	1100	0.99	0.76
$As_{60}Se_{40}$ annealed	750	0.88	0.74

It is obvious that *in-situ* photodarkening kinetics are quite similar in $As_{40}Se_{60}$ and $As_{50}Se_{50}$ films, revealing a strong tendency to non-dispersivity (β values are slightly deviated around 0.6), while photodarkening in $As_{60}Se_{40}$ films corresponds mainly to single-exponential rule with β value close to 1.0. The photoinduced optical effects are accelerated (transition to smaller effective time constant τ) and attain a more stretched nature (decrease in stretching parameter β) in annealed films of all compositions, having a smaller optical band-gap due to thermally-induced long-wave shift of fundamental optical absorption edge. The photodarkening is maximal and faster in $As_{50}Se_{50}$ films independently on their pre-history.

In general, all the above tendencies in studied thin films agreed with penetration depth dependence: the greater penetration depth of pumping light, the smaller non-dispersivity in the photodarkening kinetics. Nevertheless, we suppose, especially based on the observed difference in the normalized kinetics shown in right Fig. 3, that photodarkening in $As_{60}Se_{40}$ films probably differ in its origin from other films. This finding is in unison with conclusion on photoinduced transformations of cage-like As_4Se_3 molecular clusters [5] possible in thin films of this composition.

To justify these conclusions on a decisive role of penetration depth effects for *in-situ* photodarkening kinetics in thin chalcogenide films, we cardinally change general direction of our experiments by selecting thin films of one chemical composition ($As_{60}Se_{40}$), but varying their thicknesses. Table 2 contains the results of our modelling. The penetration depth d^* of pumping He-Ne-laser beam for these films calculated as inverse of absorption coefficient in respect to eq. (3) was estimated to be 3.7 μm before photoexposure and only near 0.5 μm in after-illuminated saturated state. So we can suppose that in the initial under-illumination state, these films behave as non-dispersive ones, revealing photodarkening kinetics close to single exponential. But with photoexposure duration, this kinetics attains a character non-exponentionality because of strong decrease in the penetration depth d^*. In other words, it means that β value to a great extend is defined by photoinduced modulation deepness in optical properties of studied thin films.

Table 2. Fitting parameters in eq. (1) for $As_{60}Se_{40}$ films of different thicknesses.

d, μm	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 can see from Table 2, when the film thickness d is smaller than penetration depth d^*, the dispersion parameter $\beta=1$ is obtained, 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 nature and hence it can be presented by a stretched exponential relaxation function. It is clear the dispersive photodarkening kinetics obeying stretched exponential function (7) is observed in relatively thicker films, while in thinner films this kinetics corresponds to single exponential function, justifying that photostrucrural transformation itself is nondispersive in nature.

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 associated with decrease in d^*).

In this view, it should be with a necessity noted that preferential kinetics of post-illuminated self-bleaching observed in thin As_2S/Se_3 films affected by pumping light of high intensity has no any relation to the real nature of *in-situ* or *ex-situ* photodarkening in these films. This kinetics corresponds exceptionally to structural relaxation responsible for some specific intensity-related instabilities, but not to principal photodarkening effect, which can be more complicated in a nature evolving changes of short- and long-range near-neighbor interactions.

4. Conclusions

The *in-situ* photodarkening in amorphous arsenoselenide As-Se films is non-dispersive in nature, its kinetics description on thickness, thermal pre-history and chemical composition being governed by penetration depth of pumping light beam in respect to film thickness. The greater penetration depth of pumping light, the smaller non-dispersivity in the resulting photodarkening kinetics.

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References

[1] V. M. Lyubin, Photographical processes on the base of vitreous chalcogenide glasses. In: Nonsilver photographical processes. Edited by A.L. Kartuzhanslii, Leningrad, Khimia, 1984.
[2] S.B. Gurevich, N.N. Ilyashenko, B.T. Kolomiets, V.M. Lyubin, V.P. Shilo, Phys. Stat. Sol. **A26,** K 127 (1974).
[3] S. Ovshinsky, Phys. Stat. Sol. **B246**, 1741 (2009).
[4] A. Ganjoo, H. Jain, Phys. Rev. **B74**, 024201-1-6 (2006).
[5] H. Pribylova, K. Antoine, M. Vlcek, H. Jain, Thin Solid Films **519**, 3950 (2011).
[6] N. Nakagawa, K. Shimakawa, T. Itoh, Y. Ikeda, Phys. Stat. Sol. **C7**, 857 (2010).
[7] K. Shimakawa, N. Nakagawa, T. Itoh, Appl. Phys. Lett. **95**, 051908-1-3 (2009).
[8] J.C. Phillips, J. Stat. Phys. **77**, 945 (1994).
[9] M. Potuzak, R.C. Welch, J.C. Mauro, J. Chem. Phys. **135**, 214502-1-7 (2011).
[10] A.R. Barik, K.V. Adarsh, Naik Ramakanta, R. Ganesan, K.S. Sangunni, Zhao Donghui, H. Jain, Phys. Stat. Sol. **C8**, 2770 (2011).
[11] L. Tichy, H. Ticha, P. Nagels, R. Callaerts, R. Mertens, M. Vlcek, Mat. Lett. **39**, 122 (1999).
[12] P. Nagels, R. Mertens, L. Tichy, Mat. Lett. **57**, 2494 (2003).
[13] M. Munzar, L. Tichy, Phys. Stat. Sol. (RRL), **1**, R74 (2007).
[14] M. Munzar, L. Tichy, J. Mater. Sci.: Mater. Electron. **18**, S252 (2007).
[15] M. Kincl, K. Petkov, L. Tichy, J. Optoelectron. Adv Mater. **8**, 780 (2006).
[16] H. Klym, V. Balitska, O. Shpotyuk, M. Vakiv, Chemia i Ochrona Srodowiska **10,** 33 (2005).
[17] M.S. Iovu, V.G. Ciorba, E.P. Colomeico, M.A. Iovu, NA.M. Nastase, A. Prisacari, M. Popescu, O.I. Shpotyuk, J. Optoelectron. Adv. Mater. **7**, 2333 (2005).
[18] M. Bertolotti, F. Michelotti, V. Chumash, P. Cherbari, M. Popescu, S. Zamfira, J. Non-Crys. Sol. **192-193**, 657 (2002).
[19] V.A. Mashkov, Wm.R. Austin, Lin Zhang, R.G., Leisure R.G., Phys. Rev.

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