Photosensitivity Color-Center Model for Ge-Doped Silica Preforms

C. L. Janer, A. Carballar, L. Navarro, J. L. Galo, and R. M. Rubio

Departamento de Ingeniería Electrónica, Escuela Técnica Superior de Ingeniería,
Universidad de Sevilla, 41092 Seville, Spain

Abstract: A new photosensitivity physical model for Ge-doped silica preforms based on color-center photoreactions is presented. Simulation results are in close agreement with experimental results obtained by several condensed matter physics research groups working in this field, suggesting that the photoreactions of this model may, indeed, describe the physical processes involved in Ge-doped silica preform photosensitivity. The proposed photosensitivity model is defined by two differential equations that describe the temporal evolution of a set of color-center concentrations. The first is a modification of a very fast reversible reaction previously proposed by Fujimaki *et al.*, where the reaction precursor has a different chemical structure (it is a neutral oxygen divacancy *NODV* unrelated to the previously proposed germanium lone pair center *GLPC*). The chemical structure of this precursor defect explains the generation of nonintrinsic neutral oxygen monovacancy (*NOMV*) color centers. These centers are transformed into *GeE′* defects by means of a second nonlinear reaction. This justifies the slow increase in the absorption peak experimentally measured at 6.3 eV, which had no satisfactory explanation.

Index Terms: Optical properties of photonic materials, fiber gratings, modeling.

1. Introduction

The refractive index of Ge-doped optical fibers exhibits a permanent change when exposed to ultraviolet light, typically in the range 240-250 nm [1]. This physical phenomenon resulted in the development of fiber Bragg gratings, which have strongly contributed to modern optical telecommunication systems [2], [3]. The physics involved in the photosensitivity phenomenon have not yet been clarified, although the general consensus is that photosensitivity is initiated through photochemical reactions of color centers [4], [5] that give way, at a later stage, to densification of the UV irradiated glass [6]–[8].

In this paper, we describe a new comprehensive model for the photochemical reactions that take place in Ge-doped silica *preforms* fabricated by traditional means (we explicitly exclude sol-gel samples, since this is a thin-film fabrication process [9]–[12] where densification may play a significant role). This model generates results that are in close agreement with the published experimental results. *Since the simplest case of photosensitivity in silica preforms takes into account a single dopant (Ge) and since this case has not yet been adequately explained, we will neither consider any other co-dopants nor try to model the densification related photosensitivity processes.* We concentrate on preforms to avoid the complications that occur in fibers and in thin-film samples (where the strain distributions may enhance the densification processes).

Most fiber photosensitivity models currently in use are purely empirical [13]–[17]. However, we believe that the results already published by some condensed matter physics research groups [18]–[34] in this field provide the key to understanding the first underlying physical mechanisms (color-center photoreactions). Therefore, the physical phenomena responsible for the photosensitivity of Ge-doped preforms are analyzed and modeled in this work. As we have already explained, due to the complexity of the problem, we have decided to consider only the simplest case of a Ge-doped preform with no co-dopants. This is considered as an initial step in the development of photosensitivity models for optical fibers.

The model presented in this paper reproduces the changes induced in the absorption spectra of conventional Ge-doped silica preforms while the glass is being irradiated with UV light [5], [10], [22], [26], [29], usually using a switched excimer laser. The photo-induced changes in the absorption spectrum are uniquely related to the refractive index change by the Kramers-Kronig relations. Consequently, we will only consider and present absorption spectrum changes. We present simulation results that corroborate the validity of our color center model.

2. Color-Centers

Ge-doped silica preforms exhibit photosensitivity because during fabrication some of the Ge atoms do not react to produce GeO_2 stoichiometric tetrahedrons [5] (due to an insufficient oxygen supply during the process) i.e., because oxygen deficiency defects are present in the silica preform. The number of these defects critically depends on the Ge concentration and the oxygen pressure conditions during the preform fabrication [3]. Some of these defects are optically active (precursor defects) since they can absorb light (typically UV radiation) and undergo a photochemical reaction that transforms them into other defects that are also optically active (product defects). These absorption spectral changes are responsible for an increase in the refractive index at the typical wavelength where Optical Communication Systems operate ($\lambda = 1550$ nm) i.e., they are responsible for the preform photosensitivity.

There is a general consensus that there are two main precursor defects which have several features in common: they both have Ge-O bond vacancies, and, therefore they are named Neutral Oxygen Defect Centers ($NODCs$). They are both optically active centers and present an absorption peak around 5.1 eV [19] and they both leave no trace in electron-spin-resonance (ESR) measurements (i. e. they are non-paramagnetic centers). In the first defect, there is a single oxygen vacancy, and in the second one, there are two oxygen vacancies. Consequently, we will call these two defects $NOMV$ (neutral oxygen monovacancy) and $NODV$ (neutral oxygen divacancy).

Some research groups have presented convincing evidence suggesting that the Ge tetrahedrons may tend to form clusters in the preform [24], [26] and, consequently, Ge-Si bonds only play a minor role in the photochemical reactions. They took transmission electron microscope (TEM) photographs where particles of size in the 6 to 10 nm range can be clearly seen. They performed electron paramagnetic resonance spectra measurements (EPR) that strongly suggest that these particles are made of GeO_2. This would reflect the fact that the soot is primarily composed of GeO_2 and SiO_2 fine glass powders that are not homogenized at nano-metric scales in the subsequent preform consolidation process. *Consequently, we will neglect the role played by the possible Ge-Si bonds*.

It is generally agreed that the chemical structure of $NOMVs$ is the one described by Hosono *et al.* in [19]. However, there is no such consensus for the $NODVs$. We assume that the chemical structure of the $NODV$ is similar to the one proposed by Tsai *et al.* in [21]. Tsai *et al.* [2], [21] provide experimental evidence that support this hypothesis. Quoting a sentence of the abstract: "The observation of the absorption coefficient increased as the square root of the Ge concentration demonstrates that the 5.16eV band is not related to two-coordinated Ge defects but it is an oxygen deficiency center of the divacancy type associated with Ge".

This point of view is controversial since many researchers working in this field assume a different chemical structure (the $GLPC$, from germanium lone pair center) to the $NODV$. However, for reasons that will become clear later, we believe that a chemical structure similar to the one proposed by Tsai *et al.* corresponds to the $NODV$ defect.
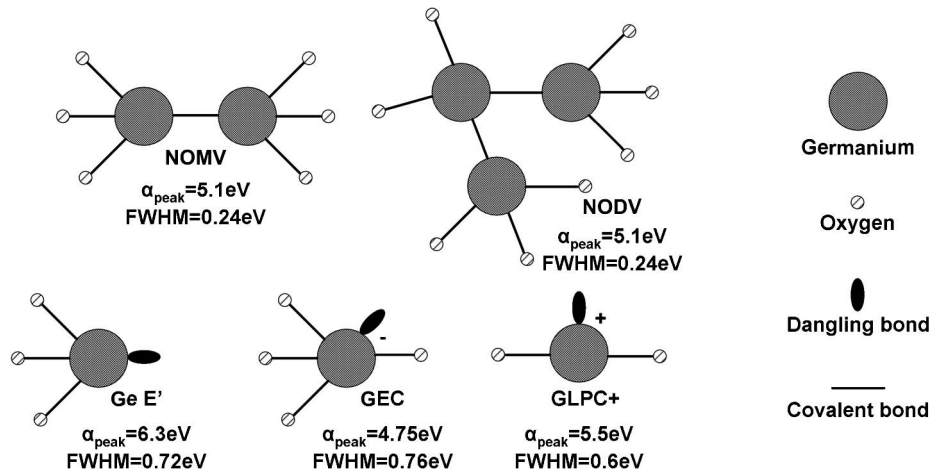
Fig. 1. Color centers.

The chemical structures and assigned absorption bands for the proposed defects (precursors and products) are shown in Fig. 1. Please note that the assumptions made for the precursor centers *NOMV* and *NODV* have been taken from references [19] and [21], respectively.

For the color-center products the following assumptions have been made:

1) The color center *GeE'* is responsible for the 6.3 eV absorption band [17], [26], [29].
2) GeO_2^- defect centers differing only in the number of next-nearest-neighbor germanium (what we call *GEC* centers) should be assigned to the same absorption peak [27], [30], [31]. The *GEC* center is responsible for the 4.75 eV absorption peak [25], [27].
3) The $GLPC^+$ center is associated to the 5.5 eV absorption peak [27]. This defect, like the *GeE'* and *GEC* ones, is a paramagnetic center since it has dangling bonds and therefore, it can be identified and its concentration determined using EPR measurements [25], [27].

Again, assumptions 2 and 3 are controversial, since there are also other research groups [18], [34] claiming that the 4.75 eV and 5.5 eV absorption peaks are related to two energetically in-equivalent configurations of the *GEC* center. Both groups provide experimental results that seem to corroborate their claims. We have taken a pragmatic approach: we have simply chosen the option that permits us to define a model that reproduces the empirical data (the measured absorption spectral changes).

The peak positions and full width half maximum values, FWHMs, of the different absorption bands have been taken from [10] and are shown in Fig. 1.

3. Precursors Absorption Band Characteristics and Photochemical Reactions

3.1. One-Photon Reactions (Hg Lamp Irradiation)

It has been experimentally verified that *NOMVs* present an absorption peak at 5.1 eV and that this peak can be almost completely bleached by a long exposure (typically ten days) to an Hg lamp, through the absorption of a single UV photon. It is generally accepted [19] that the products of this reaction are a *GeE'* defect (whose absorption band is around 6.3 eV), a GeO_3^+ defect (which is optically inactive) and a free electron, as shown in Fig. 2.

The formation of the *GeE'* centers from *NOMV* centers are described by a rate of conversion [19]

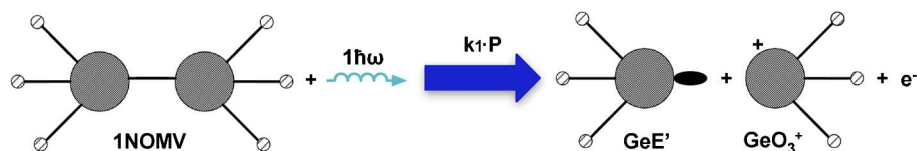$$\frac{d[NOMV]}{dt} = k_1 P([NOMV]_0 - [NOMV]) \tag{1}$$

Fig. 2. *NOMV* one-photon bleaching reaction. The term $k_1 \times P$ indicates that the kinematics is proportional to the photon flux density (the optical process is linear).
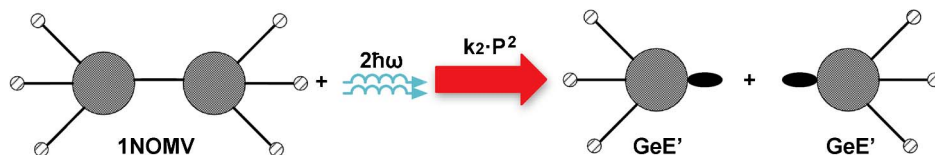

Fig. 3. *NOMV* two-photon bleaching reaction. The term $k_2 \times P^2$ indicates that the kinematics is proportional to the square of the photon flux density (the optical process is non-linear).

where $[NOMV]_0$ and $[NOMV]$ denote the concentrations before illumination and concentrations of unbleached *NOMV* after illumination at time t, respectively. P is the incident photon flux and k_1 is a rate constant depending on the Ge concentration percentage and sample temperature.

NODVs behave differently when exposed to the same light source (Hg lamp). Their absorption peak, centered also at 5.1 eV, cannot be bleached. However, an intense photoluminescence is observed at 4.3 eV and a weak one at 3.2 eV after irradiation, suggesting its decay through intermediate energy levels [22].

3.2. Two-Photon Reactions (Excimer-Laser Irradiation)

In this paper, we assume that, since the *NOMV* one-photon reaction is very slow [19], it is sensible to consider that a faster two-photon reaction can take place when switched lasers are used to irradiate the samples. This optically non-linear reaction of the *NOMV* precursor defect has been included in our model, and it is represented in Fig. 3. The reason why this reaction has been proposed is that the experimentally measured dynamics in [22] of the bleaching of the *NOMV* 5.1 eV and the generation of the *GeE'* 6.3 eV bands are much faster (tens of thousands of laser shots) than the dynamics of the simulated one photon absorption reaction process (millions of laser shots in our simulations). In Fig. 3 we also propose that for each photo-bleached *NOMV* two *GeE'* centers are created, increasing the rate at which the absorption at 6.3 eV grows. The k_2 coefficient has been calculated to reproduce the dynamics of the 6.3 eV peak reported in [22].

We have modified the two-photon reaction proposed by Fujimaki *et al.* [25], [27]. We assume that the reactant is the *NODV* defect instead of the *GLPC*, as shown in Fig. 4. *NODVs* can be reversibly bleached when pulsed UV lasers are used (for example, KrF, XeCl and ArF lasers). Products (*NOMV*, *GLPC*$^+$ and *GEC*) are generated from reactants by means of a two-photon reaction and the opposite reaction takes place by the absorption of a single UV photon [25].

The following absorption band assignments for the reaction products [10], [25] have been made:

- *NOMV* is related to the 5.1 eV absorption band.
- *GLPC*$^+$ is related to the 5.5 eV absorption band.
- *GEC* is related to the 4.75 eV absorption band.

The reversible reaction of the *NODV* is complex. We propose in this paper that both the one-photon and two-photon reactions produce an intermediate compound, shown in Fig. 4, where the Ge-Ge bonds are energized and rearranged in a transition state (also called an activated complex). The chemical structure of this transition state is closely related to the *NODV* structure proposed in [21] and justifies the generation of new non-intrinsic *NOMV* in this reaction.

This *NODV* reversible reaction is usually driven by a Q-switched laser and reaches equilibrium state very quickly [25] (after a few tens of pulses) compared to the dynamics of the NOMV reaction
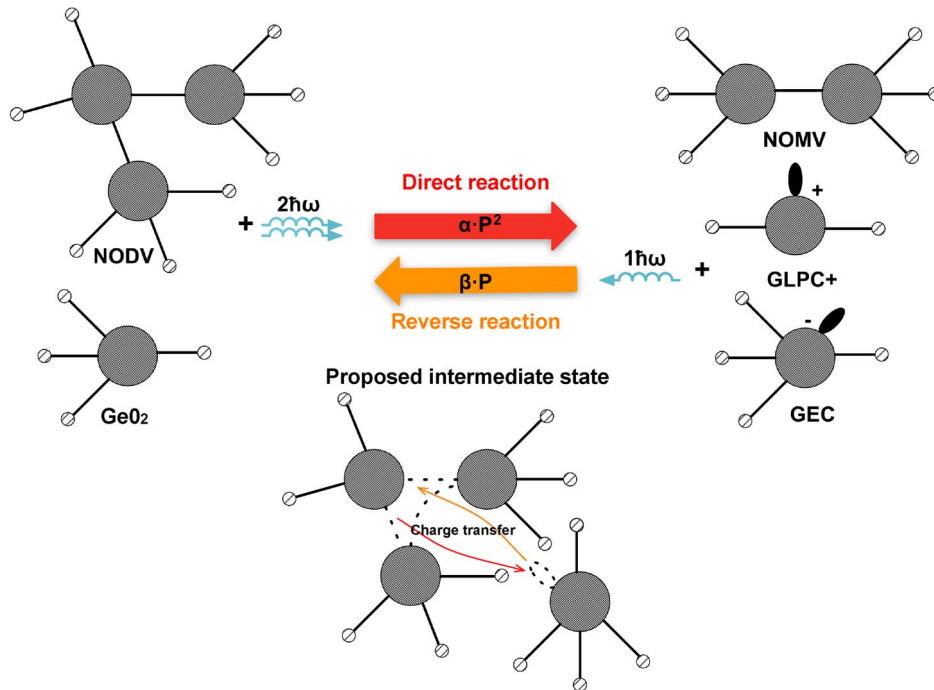
Fig. 4. NODV reversible reaction.

[22] (that typically require tens of thousands of laser pulses to be completed). For each bleached NODV (5.1 eV band) a new *NOMV* (5.1 eV band), a *GLPC*$^+$ (5.5 eV band) and a *GEC* (4.75 eV band) color-center are created. A stoichiometric GeO$_2$ molecule traps the *GLPC*$^+$ missing electron creating the *GEC* color-center. The new non-intrinsic *NOMVs* are also slowly bleached by the photochemical reaction depicted in Fig. 3.

These non-intrinsic *NOMVs* where first suggested by Essid *et al.* [29]. They provided experimental results showing that there is a linear relationship between the decrease of the 5.1 eV band associated to the oxygen divacancy defects and the increase of the 4.75 eV, 5.5 eV, and 6.3 eV absorption bands. They remarked that this fact was difficult to explain without resorting to a reaction in which the oxygen divacancy first transforms into a *NOMV* and then into a *GeE'* [29].

Following this idea, we proposed in [33] a model where we assumed that the *NODV* had the chemical structure proposed in [27] (*GLPC*) and the non-intrinsic *NOMV* defects suggested by Essid *et al.* [29] were created in a *non specified reaction*. In the model proposed in this paper, we do not use the chemical structure suggested in [27] by the authors (*GLPC*), but one which is similar to the color center proposed in [21] (denoted as *NODV* in Fig. 1). In this way, apart from the *GLPC*$^+$ center and the *GEC* center, a non-intrinsic *NOMV* is also generated (Fig. 4). This fact is essential to correctly predict the measured absorption spectral growth at 6.3 eV band reported in the bibliography [5], [10], [22], [26], [29]. This growth can be now explained by the bleaching of intrinsic and non-intrinsic *NOMVs*. This reaction is shown in Fig. 3.

4. Proposed Model

The proposed photosensitivity model for Ge-doped silica preforms is depicted in Fig. 5. The first differential equation describes the bleaching of the *NODV* defects by means of a reversible reaction similar to the one proposed by Fujimaki *et al.* [25], [27]

$$\frac{dN_p(t_1)}{dt_1} = -\alpha P^2 N_p(t_1) + \beta P N_i(t_1), \qquad 0 \leq t_1 \leq \tau \qquad (2)$$
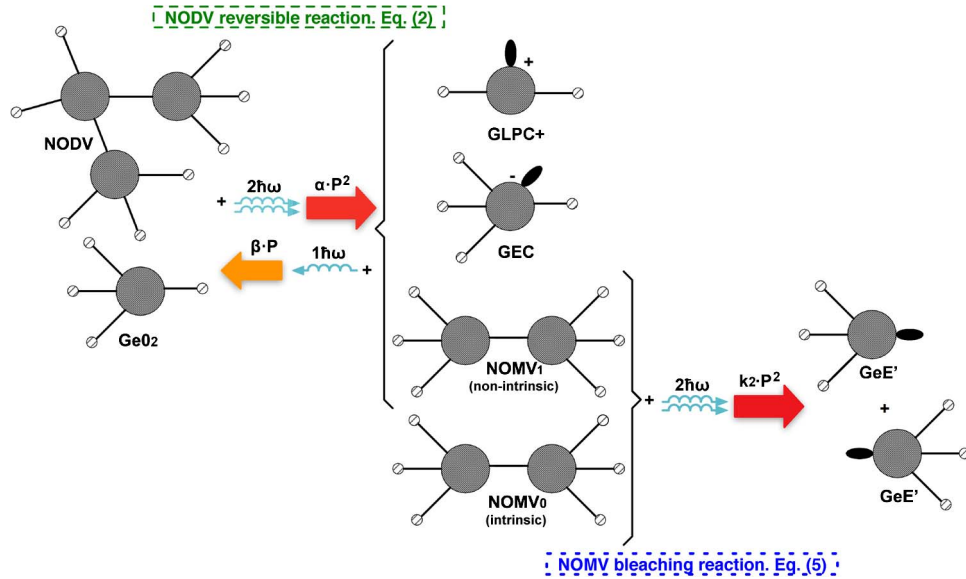
Fig. 5. Proposed model for the photosensitivity of Ge-doped preforms.

where the different color-center concentrations are

$$N_p(t_1 = 0) = [NODV_0]$$
$$N_p(t_1) = [NODV]$$
$$N_i(t_1) = [NOMV_1] = [GLPC^+] = [GEC]. \tag{3}$$

P represents the photon-flux density and α and β are constant model parameters taken from [25] that do not depend on P. This fast reversible reaction typically reaches equilibrium after a few tens of UV laser pulses. Time τ is long enough so that this reaction reaches its equilibrium state. The defect concentration at $t_1 = \tau$ are

$$N_p(t_1 = \tau) = [NODV]_\tau$$
$$N_i(t_1 = \tau) = [NOMV_1]_\tau = [GLPC^+]_\tau = [GEC]_\tau. \tag{4}$$

In this reaction, non-intrinsic $NOMV$ defects are generated (denoted as $NOMV_1$ in Fig. 5). As a consequence of the generation of these non-intrinsic $NOMVs$, the 6.3 eV absorption peak grows faster and reaches the large measured values reported in [10], [22], [29].

The second differential equation describes the irreversible non-linear bleaching of the $NOMV$ centers (both intrinsic and non-intrinsic)

$$\frac{dN(t_2)}{dt_2} = (k_2 P^2)[N_0 - N(t_2)], \qquad 0 \simeq \tau \leq t_2 \leq T, \quad \tau \ll T \tag{5}$$

where

$$[NOMV(t_2)] = N_0 - N(t_2)$$
$$[GeE'(t_2)] = 2N(t_2)$$
$$N_0(t_2 = \tau) \simeq [NOMV_0] + [NOMV_1]_\tau. \tag{6}$$

Notice that (2) is not affected by (5) since all reactions are local (that is, all defects are located at a given place of the preform and are not free to move from their locations). αP^2 is proportional to the probability of an existing $NODV$ being transformed into the products. Similarly, βP is proportional to the probability of the existing three reaction products reacting to produce a $NODV$. If $NOMVs$

TABLE 1

Simulations parameters

Reactions parameters [a]	Value	Units
α	1.0×10^{-42}	$cm^4 \times s$
β	1.3×10^{-18}	cm^2
k_2	2.0×10^{-43}	$cm^4 \times s$
Cross-sections [b]	Value	Units
σ_{NOMV}	4.13×10^{-17}	cm^2
σ_{NODV}	13.80×10^{-17}	cm^2
σ_{GLPC+}	11.10×10^{-17}	cm^2
σ_{GEC}	4.58×10^{-17}	cm^2
$\sigma_{GeE'}$	6.24×10^{-17}	cm^2

[a]From Phys. Rev. B 53, 9859 (1996) [25]
[b]From J. Appl. Phys. 85, 3413 (1999) [10]

TABLE 2

Precursor defects initial concentrations

Defect concentrations [a]	Value	Units
$[NOMV]_0$	3.16×10^{16}	cm^{-3}
$[NODV]_0$	6.30×10^{17}	cm^{-3}
Defect concentrations [b]	Value	Units
$[NOMV]_0$	1.33×10^{17}	cm^{-3}
$[NODV]_0$	3.29×10^{17}	cm^{-3}
Defect concentrations [c]	Value	Units
$[NOMV]_0$	9.68×10^{16}	cm^{-3}
$[NODV]_0$	1.45×10^{17}	cm^{-3}

[a]From Phys. Rev. B vol. 52, pp. 16661 (1995), Fig.1 [22]
[b]From J. Non-Crys. Solids vol. 246, pp. 39 (1999) [29]
[c]From J. Appl. Phys. vol. 85, pp. 3413 (1999) [10]

disappears by means of the second reaction (5), the *GLPC*$^+$, *GEC*, and *NODV* concentrations remain unchanged. This irreversible reaction is very slow compared to the previous one. The value of k_2 has been fixed so that the calculated absorption dynamics coincide with those presented by Nishii *et al.* in [22].

The set of cross-sections that relate the absorption coefficients to the defect concentrations are given in Table 1 and have been taken from [10].

5. Simulation Results

The initial concentrations of the precursor defects for these simulations have been obtained from references [10], [22], [29] and are shown in Table 2. Defect concentrations have been calculated taking into account that an Hg lamp can only bleach the *NOMV* defects, leaving the *NODV* defects unaffected (10 days—230 hours—are considered to be an exposure time long enough to bleach the total amount of *NOMV* defects [22]).
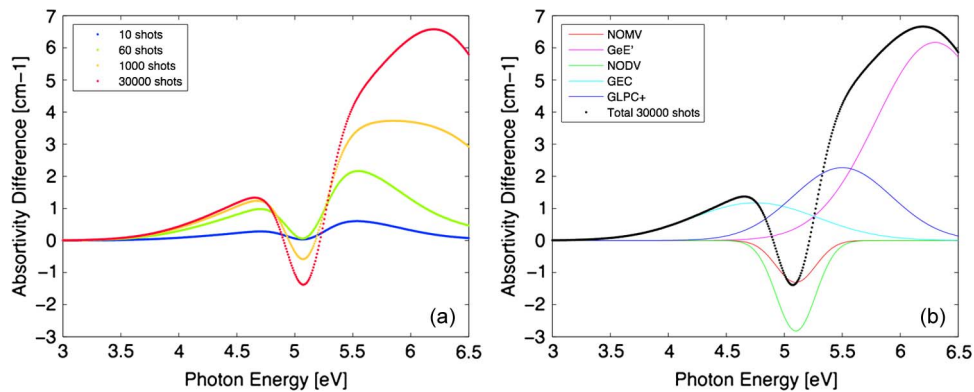
Fig. 6. Simulation of the difference absorption spectra of $10GeO_2-90SiO_2$ glasses before and after irradiation with a KrF laser (10 mJ/cm^2/pulse at 5.0 eV; t_{ON} = 20 ns) after 10, 60, 1000, and 30 000 shots: (a) Absorptivity dynamic evolution; and (b) Gaussian-decomposed bands for the steady-state condition. For comparative purposes, the experimental results can be consulted in Ref. [22].
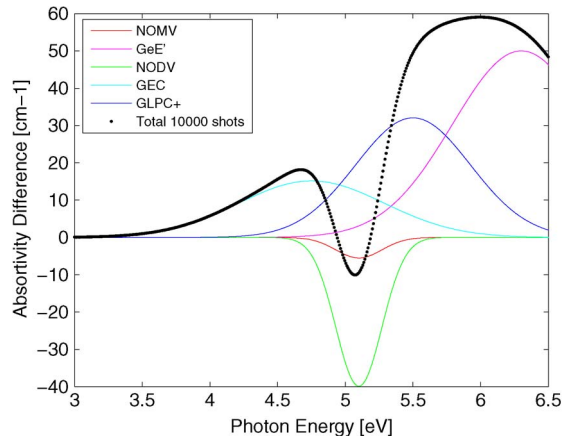

Fig. 7. Simulation of the difference absorption spectra of 3 GeO_2-97 SiO_2 glasses before and after irradiation with a KrF laser (150 mJ/cm2/pulse at 5.0 eV; t_{ON} = 20 ns) for the steady-state condition, showing in detail the separated Gaussian components. For comparative purposes, the experimental results can be consulted in Ref. [29].

The proposed model successfully reproduces the experimental results achieved by Nishii *et al.* [22]. To the best of our knowledge, this is the only group that reports a photosensitivity dynamic evolution. They used a relatively low photon flux density laser in their experiments so that the obtained spectral absorptivity difference is rather low (the photon flux density was 10 mJ/cm^2/pulse and the light pulse duration 20 ns). In Fig. 6(a) the simulated total absorptivity spectral change has been plotted for 10, 60, 1000, and 30 000 excimer KrF (5 eV) laser shots. This figure shows that the reaction described by equation (2) reaches its steady-state in less than 100 laser pulses. Reaction (5) slowly bleaches the *NOMV* (both intrinsic and non-intrinsic) defects absorption band producing an increase in the 6.3 eV absorption peak related to the generation of *GeE'* defects. Please note that during the photosensitivity dynamic evolution, the absorption peak at 5.1eV always decreases due to the difference between the cross-section values of the *NODV* and *NOMV* color-defects (see Table 1). In Fig. 6(b), the Gaussian decomposition is shown so that the contribution of each color-center to the total absorptivity change can be seen for the steady-state conditions.

In Fig. 7 only the steady-state conditions are represented since no information about the experimental absorptivity dynamics is provided by Essid *et al.* in [29]. The total absorptivity differential spectrum is relatively large even though the GeO$_2$ concentration is rather low (3%). This can be
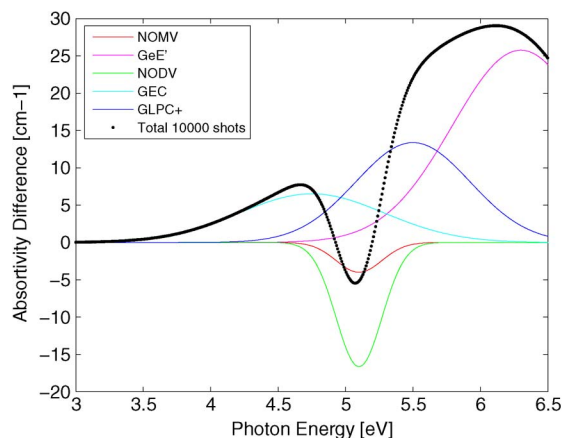
Fig. 8. Simulation of the difference absorption spectra of 9.8 $GeO_2-90.2$ SiO_2 glasses before and after irradiation with a KrF laser (100 $mJ/cm^2/pulse$ at 5.0 eV; $t_{ON} = 20$ ns) for the steady-state condition, showing in detail the separated Gaussian components. For comparative purposes, the experimental results can be consulted in Ref. [10].

explained by the facts that the *NOMV* precursor defect concentration is larger than in the previous case, the *NODV* precursor defect concentration has the same order of magnitude and the laser power is much higher $(150\ mJ/cm^2/pulse)$ and, therefore, the reversible reaction (5) generates more products than in the previous experiment. The Gaussian decomposition is also depicted in this case so that the contribution of each color-center to the total absorptivity change can be seen. It should be reminded that the number of precursor defects depends not only on the Ge concentration but also on the oxygen pressure conditions during the preform fabrication [3].

Finally, we have also been able to reproduce the steady-state results reported by Shigemura *et al.* [10]. They present steady-state absorptivity changes, both for preform and sol-gel samples. Our model correctly reproduces the preform experimental results (see Fig. 8). In this case, the used KrF laser had a 100 $mJ/cm^2/pulse$ photon flux density. In all three cases there is a close agreement between our simulations and the experimental results.

6. Conclusion

In this paper, we have proposed a physical model that correctly reproduces the photosensitivity of Ge-doped silica preforms. Two different reactions govern the evolution of the color-center concentrations. The first one is a very fast reversible reaction that describes the bleaching of the *NODV* defects. In this reaction (a similar reaction had been previously proposed), we have introduced significant changes that explain the appearance of new (non-intrinsic) *NOMV* color-centers. The transformation of the *NOMV* color-centers into *GeE′* defects by the second reaction explains the experimentally observed slow and large increase in the absorption peak observed at 6.3 eV which was not satisfactorily explained in previous models. The simulation results suggest that the proposed photochemical reactions may very well describe the physical processes responsible for the Ge-doped perform photosensitivity.

Acknowledgment

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