

COMPARISON OF PHOTOINDUCED ATOM DISPLACEMENTS IN GLASSES AND POLYMERS

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When exposed to visible-UV light, photoinduced atom displacement (PAD) may occur in certain inorganic glasses as well as polymers, leading to similar changes in their optoelectronic and structural properties. An understanding of PAD is important for the use of these materials in photonic applications such as optical storage, CD-RW, opto-mechanical transducers, etc. In both classes of materials, PAD is caused by a combination of electronic excitation and subsequent response of the structure to the excited state configuration. There are indications of photoinduced localized atomic restructuring as well as long-range diffusion, which require bond-breaking. In spite of the initially homogeneous, isotropic structure, the photoinduced effects can be anisotropic, depending on the direction of polarization and/or the direction of light propagation. In general, the PAD in polymers is much larger but less stable than that in glasses, presumably due to the greater adaptability of polymer structure to the optically created polarization and other stresses. A combination of these characteristics in a single glass-polymer or organic-inorganic material is likely to yield superior photoinduced properties. A comparative overview of PAD in inorganic glasses and polymers is presented in this paper.

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1. Introduction

A priori, one does not expect any significant photoinduced atom displacement (PAD) in solids due to simple collision with photons, because the latter have negligible momentum and the atoms are massive as well as strongly bonded to neighbors. However, contrary to the expected negligible PAD from direct collision with photons, there are well known examples in nature and technology where atomic structure is altered permanently by exposure to light e.g. in photosynthesis, photography, etc. There are recent reports of a variety of novel photoinduced phenomena and changes in various physical properties of selected materials, which obviously imply a change of structure and large displacement of atoms due to exposure to light of some special frequencies. For example, the experimentally observed photoinduced chemical modification [1] and photoexpansion [2] of chalcogenide glasses by bandgap light, or photoalignment of liquid crystals by the light of certain frequency [3] must be accompanied by atom displacements. Photocells and next generation optical recording in compact discs are based on photoinduced changes in electrical conductivity and reflectance, which illustrate the wide potential of photoinduced phenomena in today's technology.

The precise observations of PAD are relatively recent, and they have yet to reach the commercial success of the primarily electronic phenomena. Notwithstanding, they have the potential of introducing novel photonics applications where photons will replace the function of electrons such as in optical switches, opto-mechanical transducers, nano-positioners, optical actuators, etc.

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Photoalignment of chromophores in polymer matrix, especially the azo polymers, has attracted much attention for high density erasable memory applications (e.g. compact disc – recordable and rewritable i.e. CD-R and CD-RW), which are expected to replace currently used organic polymers that show a change in optical properties from photo-thermal treatment. For such applications, key material requirements are: thermal stability, resistance to fatigue from write-erase cycles, fast response, high sensitivity and nondestructive readout capability. The photoinduced atom movement directly or indirectly determines these characteristics and, hence, is a key to the functioning of the new photochromic memories and switches. At present the polymers lack sufficient reliability. Hence, there is parallel interest in inorganic glasses, especially the chalcogenides that show similar photoinduced phenomena and PAD, but of a smaller magnitude. In this paper we present an overview, comparing photoinduced atom displacements in these two classes of materials; readers interested in specific aspects of these topics are referred to exhaustive reviews [3-15]. Hopefully, their comparative understanding will help in the development of superior materials for a given application. Here we will focus on experimental observations of the atom displacement rather than optical properties, which have been investigated extensively as summarized in these reviews. The scope of this article covers the novel photoinduced effects leading to new technology. It is in the spirit of contributions made by Stanley Ovshinsky who discovered photoinduced phase change in chalcogenide glass. He investigated its fundamentals with technological applications in mind [16], which have ultimately led to the erasable optical memory technology for multi-media using glass-crystal phase transformation in an Ag-In-Sb-Te alloy [17].

In general, the PAD in the materials of interest occurs with the intermediation of electrons rather than by a direct collision with the photons. To begin with, an electron in the solid is excited to a higher energy state by absorbing photon.ⁱ If this absorption process causes spatial displacement of charge, the solid is polarized with respect to the dark state, causing a displacement of ions in the vicinity of the excited electron [18]. If the electronic transition is between two well-defined levels, one may expect resonant absorption of the photons that have frequency corresponding to the energy difference between the two levels. The ensuing atom displacement is then selective to that specific frequency of light – the polarization direction of the incident light may not be important. Such isotropic changes in the structure of the material lead to scalar effects like photodarkening in chalcogenide glasses, photoinduced embrittlement of polymers, etc. By contrast, if the structural change correlates with the direction of the polarization of the incident light (i.e. its electric field vector, \mathbf{E}), the result is termed a photoinduced vector effect in the glass literature. Polymers also show polarization dependent effects but the use of term ‘vector’ is not common in that context. Such anisotropic changes in a homogeneous, isotropic glass or polymer are indeed intriguing.

The magnitude of an atom’s displacement would depend on how sensitive it is to the field of photoinduced polarization. An atom tightly anchored by its neighbors will show minimal displacement, but under similar polarization the same atom, if loosely bonded to some other neighbors, may undergo significant displacement. Obviously, if the excitation of electron does not create sustained polarization for the time sufficiently long for an ion to respond, photoinduced atom displacement will not occur by this mechanism. That will be the case of metals, in which usually PAD is not observed.

2. Photoinduced atom displacement in inorganic glasses

2.1 Manifestations of PAD in inorganic glasses

Common inorganic glasses are strongly bonded covalent-ionic oxide solids based on three dimensional silica network. Below the glass transition temperature (T_g), the network forming atoms are strongly anchored in place and the visible light makes no observable atom displacement. Due to the large bandgap, ultraviolet (UV) radiation is needed to generate electron-hole pairs, but even then atom displacement is relatively small. So generally the atomic structure of oxide glasses is considered

ⁱ In this paper we will not consider the effect of ionizing radiation (X-rays and gamma rays), which often creates color centers in ionic and covalent solids.

stable against exposure to light. Only when the fluence of UV light (from excimer laser) is large, one may be able to detect PAD. Both because of its role as the most common constituent of glasses and use in optical fiber communication, the effect of UV radiation on silica has been investigated [19-26]. In general, silica undergoes compaction given by the fractional change in volume (V) [25]:

$$-\Delta V/V = a(F^2 N/t)^b \quad (1)$$

where F is the peak fluence of the UV laser beam ($\lambda = 248$ and 193 nm), N is the number of pulses in millions, and t is a measure of the laser pulse duration. The empirical parameter b is ~ 0.6 for both wavelengths, but a is 0.43 for $\lambda = 193$ nm and 0.043 for $\lambda = 248$ nm. However, recent investigations at low fluences show photoinduced expansion instead, indicating the presence of two competing processes involving opposite photoinduced atom displacements [25]. The expansion of silica is now shown to arise from the presence of hydrogen impurity [27,28]. As mentioned above, the magnitude of the compaction or the expansion is rather small. For example, 2.2×10^8 pulses of $\lambda = 248$ nm laser at 10 mJ/cm^2 /pulse in a silica heavily-doped with hydrogen, or 6.4×10^6 pulses at 13 mJ/cm^2 /pulse in a relatively pure sample, produced about 1 ppm expansion and compaction, respectively [25]. Notwithstanding the imperceptible change in sample dimensions, UV irradiation of pure and doped silica causes a significant change in refractive index i.e. photorefraction. Due to its application in making Bragg gratings [29-31], the associated photoinduced defects have been investigated extensively by spectroscopic methods [32,33], but the nature of atom displacement has not been determined. Very recently, a photoinduced birefringence by UV light has been reported indicating that, in addition to isotropic volume change, there should be also a polarization dependent anisotropic change in the density.

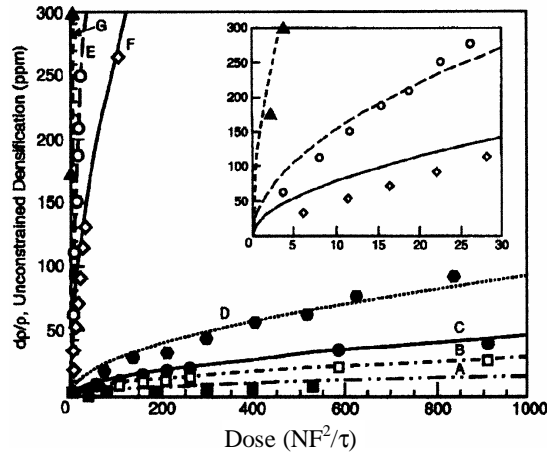


Fig. 1. Effect of glass composition on photoinduced densification of binary silicate glasses. Fractional density increase ($\Delta\rho/\rho$) is shown as a function of dose for seven silica samples: A. Dry silica, B. and C. Corning HPFS silica, D. 7% P_2O_5 - SiO_2 , E. 20% GeO_2 - SiO_2 , F. 9% B_2O_3 - SiO_2 , G. 20% B_2O_3 - SiO_2 [26].

Densification of silica is strongly affected by the addition of a second component [26]. Fig. 1 compares the fractional increase in the density of several silicate glasses as a function of the dose of 193 nm UV light. It is found that the densification rate increases as the glass becomes softer by the addition of the second oxide to SiO_2 . Accordingly, an inverse correlation is observed between the photoinduced densification rate and the annealing point (the temperature where viscosity = 10^{12} Pa.s), which is a measure of stress relaxation or the ability of glass network to respond to an external stress.

In comparison to oxides, the glasses based on chalcogens (e.g. Se, sulfides or selenides of Ge, Sb or As, etc.) are much more sensitive to light, especially if the photon energy $h\nu \approx$ bandgap energy E_g (typically 1-3 eV), where h is Planck's constant and ν is the frequency of light [11,12]. For example, the photoinduced expansion in As_2S_3 glass is orders of magnitude larger than silica, with a fractional change in length ($\Delta l/l$) of several % depending on the wavelength and intensity of light [2].

This characteristic of chalcogenide glasses has been used for fabricating micro-optical elements in As_2S_3 glass such as shown in Fig. 2 [34]. Due to the much higher sensitivity of these glasses, a variety of novel, both scalar and vector, photoinduced phenomena has been observed [11-14], which have no parallel in oxide glasses. A brief description of the various manifestations of PAD is given next:

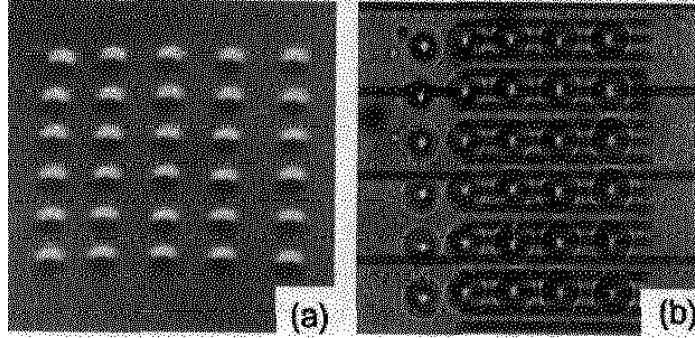


Fig. 2. Application of photoinduced densification of As_2S_3 glass by He-Ne laser for fabricating microlens array. (a) scanning electron micrograph of the film, (b) the focusing of transmitted light by these lenses. Each lens is $10\ \mu\text{m}$ in diameter and the distance between two neighboring lenses is $30\ \mu\text{m}$ [34].

(a) Photoinduced volume change

More than 25 years ago Hamanaka et al. [35] first reported that the thickness of As_2S_3 and $\text{As}_4\text{Se}_5\text{Ge}_1$ films changes by 0.39% (expansion) and -0.22% (contraction), respectively, when exposed to light from xenon lamp. The thickness of the films was recovered on annealing near the glass transition temperature; that is, the effects of irradiation and annealing were reversible. The magnitude of volume change is sensitive to the film preparation conditions, being almost ten times larger for the obliquely deposited As_2Se_3 film. Ganjoo et al. [36] have followed the volume change by in situ thickness measurements. They found that for As_2S_3 glass films illuminated by white light, there are two competing effects: a rapid increase of thickness as soon as the light is turned on, and a smaller and slower decrease due to the relaxation of structure, as shown in Fig. 3. Both effects reach plateau in due course with the net expansion observed at the end of the experiment. The ultimate magnitude of the expansion after the light has been turned off increases with the exposure time, reaching a plateau in $\sim 100\ \text{s}$ [37]. By contrast, the GeSe_2 glass films show only a decrease of thickness (see inset in Fig. 3); the structural relaxation is much slower and hence not seen here.

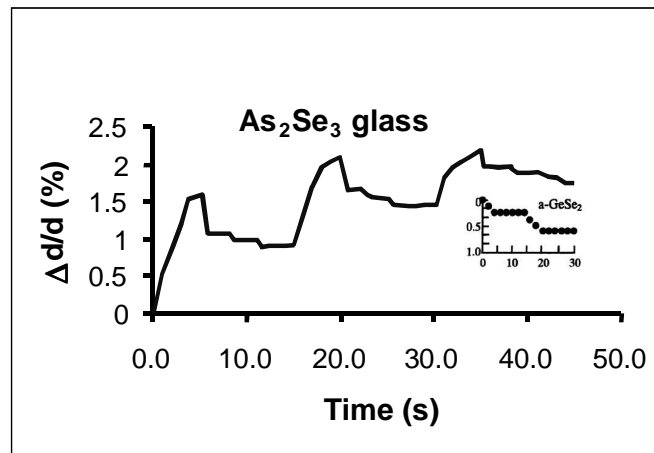


Fig. 3. Time evolution of photoinduced relative change in thickness, $\Delta d/d$, of an a- As_2S_3 film. Duration of light ON and OFF states was 5 and 10 s [36].

Although positive as well as negative photoinduced change in volume is well documented for selected chalcogenide glasses, its composition dependence has not been determined well enough to

establish correlation with the annealing point or the glass transition temperature. There is a large body of literature on photoinduced anisotropy of optical properties (absorption and birefringence) [14], which can be argued to mean an accompanying anisotropic change in expansion or compaction of the structure. However, there are no direct measurements that would indicate the magnitude of such anisotropy in photo-expansion or photo-compaction.

(b) Photoinduced Scalar Mass Transport

There are no direct measurements of the effect of light on self-diffusion, but there are clear manifestations of photoinduced mass transport in chalcogenide glasses. Most notable among these is the behavior of silver, which has been examined in As-S, Ge-S and Ge-Se glasses [15]. Three distinct types of silver transport have been observed:

(i) *Photodissolution or photodoping of silver* (also exhibited by Zn and Cd, but with some different characteristics). In this case, a film of metallic silver is plated on the surface of chalcogenide glass. On exposure to light, silver atoms diffuse into the glass as Ag^+ ions (see Fig. 4(a)) [13,38,39]. Photodissolution is thermally activated, and generally increases linearly with the intensity of light (with deviations in some cases) [40]. It is particularly effected by the light of bandgap energy [40], but can be also caused by sub-bandgap light [41]. It is viewed as a chemical or intercalation reaction between the glass and silver, which is enhanced by light absorption at the boundary of the doped-undoped regions. The primary driving force for the reaction is the electrochemical potential gradient of silver, but the kinetics is facilitated by the photo-generation of electrons and holes, and possibly photomelting [13].

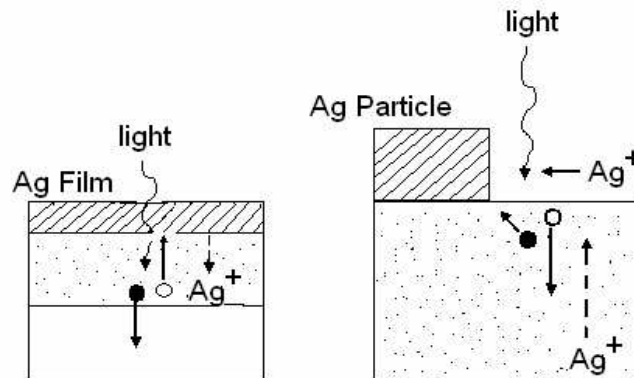


Fig. 4. Schematic of photoinduced migration of Ag^+ : (a) Photodoping or photodissolution of silver ions from metallic film on the surface. (b) Photoinduced deposition of metallic silver on the sample surface. The solid and open circles represent electron and hole created by illumination [15].

(ii) *Photoinduced surface deposition (PSD), or photoprecipitation of silver metal out of a silver chalcogenide glass*. It is the inverse of the photodissolution reaction, where Ag^+ ions initially present in the glass migrate to the surface and form metallic silver as a result of irradiation [42, see ref. 15 for a detailed review] (see Fig. 4(b)). The phenomenon is reversible on heating to T_g and, therefore, has been considered for high-density erasable optical recording devices using Ag-rich chalcogenide films [43]. PSD of silver occurs for light of energy $\geq E_g$, and increases with the intensity of light as well as with the silver content of the glass. It shows a maximum with respect to temperature, typically around the room temperature, due to competition between silver diffusivity and solubility both of which increase with temperature. However, the former helps but the latter mitigates the formation of silver particles. Like photodoping, PSD is facilitated by the creation of electron-hole pairs but with net opposite results, as compared in Fig. 4. In this case, the pair is created at the metal-free surface. The holes migrate into the glass with the concurrent migration of Ag^+ ions towards the surface, where silver particles develop by nucleation and growth.

(iii) *Photoinduced chemical modification of a silver chalcogenide glass* by exposure to bandgap light, where an Ag^+ ion concentration differential develops between the irradiated and unirradiated regions [1,44]. The irradiated region in such a glass ($\text{Ag}_{25}\text{As}_{25}\text{S}_{50}$) becomes enriched with silver ions by as much as 7 at% and persists for some time at room temperature, even after the light is removed. The concentration differential increases with temperature ($T < T_g$). Unlike the previous two effects, the concentration differential is reversible with respect to exposure to light i.e. it can be changed reversibly simply by changing the irradiation conditions. It is annealed out on heating the glass to $\sim T_g$, but not as readily as with light exposure. Photogenerated electron-hole pair is also the cause of directed Ag^+ ion migration in these glasses that are mixed hole- Ag^+ conductors. The electron mobility is small so that predominantly holes migrate from the illuminated to the dark region with a concurrent migration of Ag^+ in the opposite direction (see Fig. 5).

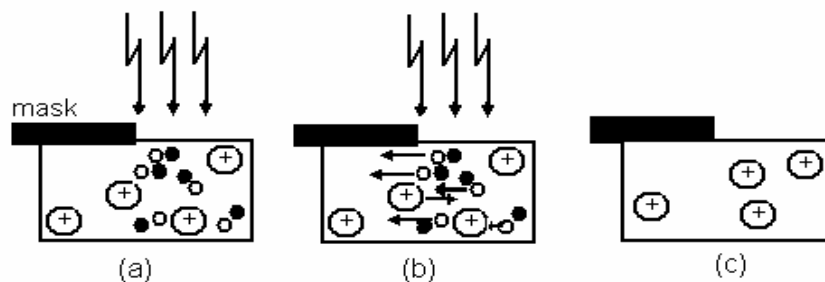


Fig. 5. Schematic description of photoinduced silver redistribution between the dark and illuminated areas. Solid, open, and positive circles represent electrons, holes, and Ag^+ ions, respectively [44]. (a) Creation of e-h pair by illumination, (b) Migration of holes from illuminated to the dark region where they are trapped. (c) Electric field driven accumulation of silver in the illuminated region.

(c) *Photoinduced Vector Mass Transport*

The above mentioned observations of mass transport are scalar effects that are isotropic and independent of the polarization of the inducing light beam. However, recently Saliminia et al. [45] have shown vector mass transport in As_2S_3 films by exposure to a fine beam of near-bandgap light. Fig. 6 shows their observation of an anisotropic relief crater created by linearly polarized beam of circular cross-section. Relatively little is known about the characteristics of such mass transport, but the authors suggest that the combination of electric field gradient, bond cleavage and creation of anisotropic defects is the source of this very interesting observation.

Besides the direct observation of optical-field induced mass transport, there are several other observations, which imply polarization dependent PAD. An early indication of photoinduced vector crystallization is given by Hanus et al. [46]. They report that the anisotropic microstructure of CuTe thin films is created partly by the polarization of laser beam that is used in its synthesis. Direct observation of anisotropic photoinduced crystallization was investigated subsequently for Se and a few other glasses [47-49]. A convenient indicator of this phenomenon is photoinduced optical anisotropy (POA), which then enhances with crystallization if conducted in the presence of polarized light.ⁱⁱ The microstructure, Raman spectroscopy, ellipsometry and X-ray diffraction show that the crystallites in these films are aligned such that Se chains are normal to \mathbf{E} field of the incident light [48,50,51]. The general belief is that polarized light preferentially supports the formation of those

ⁱⁱ POA was observed much earlier in photochromic oxide glasses containing silver halide [T.P. Seward, J. Non-Cryst. Solids 40, 499 (1980); N.F. Borrelli and T.P. Seward, Appl. Phys. Lett. 34, 395 (1979)]. In this case, the glass is first photodarkened by exposure to light that creates randomly oriented, oblate shaped silver metal colloids. On subsequent exposure to polarized light, the colloids of certain orientation absorb light preferentially and thus transform into a partially-bleached ionic state. The resulting glass with reduced darkening exhibits POA just as shown by chalcogenide glasses, but the underlying mechanism for the former does not involve vector PAD. It results simply from anisotropic absorption of light by the surface plasmons of non-spherical metallic colloids.

nuclei of trigonal Se that have their c -axis normal to \mathbf{E} . Subsequently these nuclei grow according to their specified orientation and thus lead to anisotropic crystallization. Poborchii et al. [50] suggested that preferential nucleation is due to a higher absorption of light with \mathbf{E} perpendicular to than the one parallel to the c -direction of the pre-existing molecular units. It is interesting to note that a photo-devitrified As-Se film can be photo-amorphized back by a subsequent irradiation [52,53]. In this case, the previously crystallized glass has a strained structure e.g. consisting of As_4Se_4 molecules in an As-Se film. The stresses at the film-substrate interface, and exposure to light restructure the bonds and help reestablish a polymerized structure that is amorphous.

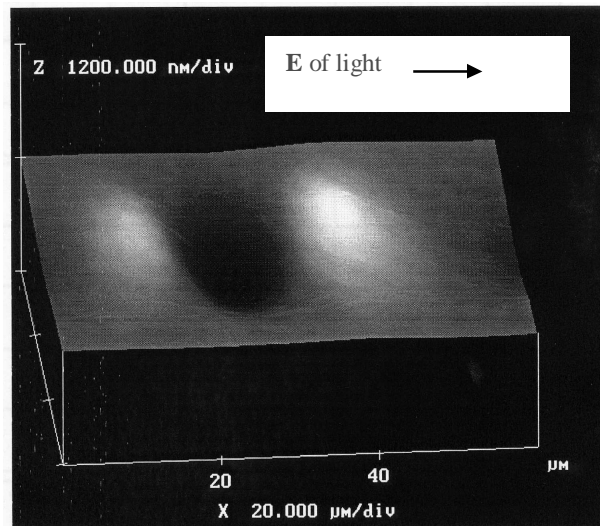


Fig. 6. Photoinduced, polarization dependent (vector) mass transport, as observed by atomic force microscopy of a As_2S_3 film exposed to linearly polarized laser beam of circular cross-section ($\lambda=514.5$ nm) [45]. Note the elliptical shape of the crater is related to the \mathbf{E} field.

Perhaps the most dramatic manifestation of polarization dependent PAD is the opto-mechanical effect reported by Krecmer et al. [54] because in this case the PAD is not only anisotropic but also temporary in the sense that it changes as the \mathbf{E} field of the light is modulated. Thus it provides a basis of opto-mechanical transducer, which would convert an optical signal directly into mechanical strain, and other novel devices. The authors exposed a thin film of AsSe on Si_3N_4 substrate to polarized light of bandgap energy. The substrate, which was the cantilever element of atomic force microscope, deflected up or down depending on whether \mathbf{E} was perpendicular or parallel to the cantilever axis, as shown in Fig. 7. Thus the film contracts along the \mathbf{E} vector of light and expands in the perpendicular direction. The authors have suggested the rotation of As-Se-As units as the cause of this effect, but its additional characteristics and direct observation of the associated PAD are needed for developing a satisfactory understanding.

2.2 Direct observations of photoinduced atom displacement in inorganic glasses

A comprehensive and direct view of the PAD in a glass can be found by comparing the radial distribution function (RDF) around the constituent atoms before, during and after exposure to appropriate light. Extended X-ray Absorption Fine Structure (EXAFS) analysis is perhaps the most appropriate technique for obtaining such information, especially for multi-component glasses, in which case it can provide the so called partial radial distribution function (PRDF) around each element separately. It gives the position of various neighbors around a specified reference atom. For elemental glass such as selenium, of course, normal X-ray scattering might be preferred, which yields information to higher coordination spheres. The second most useful technique has been Raman spectroscopy, which yields information about specific structural units and how they are affected by

the light exposure. In this section we review the information about PAD in glasses, which has been obtained using these techniques.

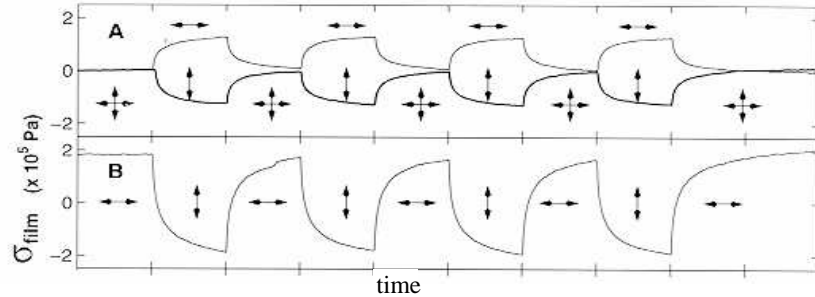


Fig. 7. Time dependence of stresses (σ_{film}) induced in an AsSe film microcantilever when exposed to He-Ne laser beam of different polarizations: horizontal, vertical and four-headed arrows indicate x-, y-, and un-polarized light, respectively. These stresses make the cantilever move down or up depending on the expansion or compression created by the laser beam [54]. Each mark on x-axis represents 5 min. In (A) unpolarized and polarized (in one of the two orthogonal directions) light was alternated; in (B) the two orthogonal polarizations were alternated.

Since the PAD in oxide glasses is expected to be rather small, there is no published report on its direct measurement by EXAFS, but some information is available from Raman scattering about the effect of UV irradiation on silica glass containing 5 or 13% germania [55]. In this case, the main conclusion is that Si(Ge)-O-Si(Ge) bond angle decreases with irradiation possibly due the decrease in the size of the rings made of SiO_4 or GeO_4 tetrahedra. Further, pre-existing Si-Ge wrong bonds are preferentially broken by UV light, which subsequently convert to Si-O-Ge bonds. Structural relaxation from this bond transformation is responsible for the photoinduced optical effects in this system.

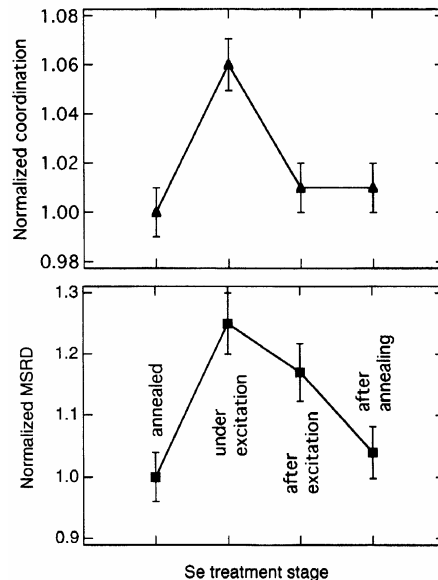


Fig. 8. Photoinduced changes in the average coordination number and mean square relative displacement (MSRD) in Se film under various conditions of exposure by bandgap light [62].

By comparison, there are several investigations of the PAD in chalcogenide glasses, starting with the work of Tanaka [56] who found that the first sharp diffraction peak in the X-ray diffraction of As_2S_3 films was reversible between exposure to light and annealing near T_g . The element-specific

PAD was first measured around the arsenic atoms in As_2S_3 films using As K-edge EXAFS [57-60]. By making use of phase-corrected Fourier transform of EXAFS oscillations, Yang et al. [57] were able to separate the correlation of a given As atom with neighboring As or Se atoms. Different PADs were responsible for the irreversible and reversible changes, which were separated by observing the first time changes when the sample was illuminated, and those observed in the subsequent illumination-annealing cycles. Major reversible changes were observed in the second coordination shell of As indicating that PADs in this glass arise from modification of bonding around the chalcogen atoms, which have flexibility due to nominal coordination with only two other atoms. Illumination enhanced the chemical disorder by increasing the concentration of wrong bonds (i.e. formation of As-As bonds at the cost of As-S bonds). There was a small increase (0.002 nm) in the average As-As distance associated with the increase of the average $\angle\text{As-S-As}$ bond angle by 0.8° , as well as broadening of its distribution by $\pm 1.8^\circ$. No change occurred in the third coordination shell, thus suggesting a change in the dihedral angle between two AsS_3 pyramids.

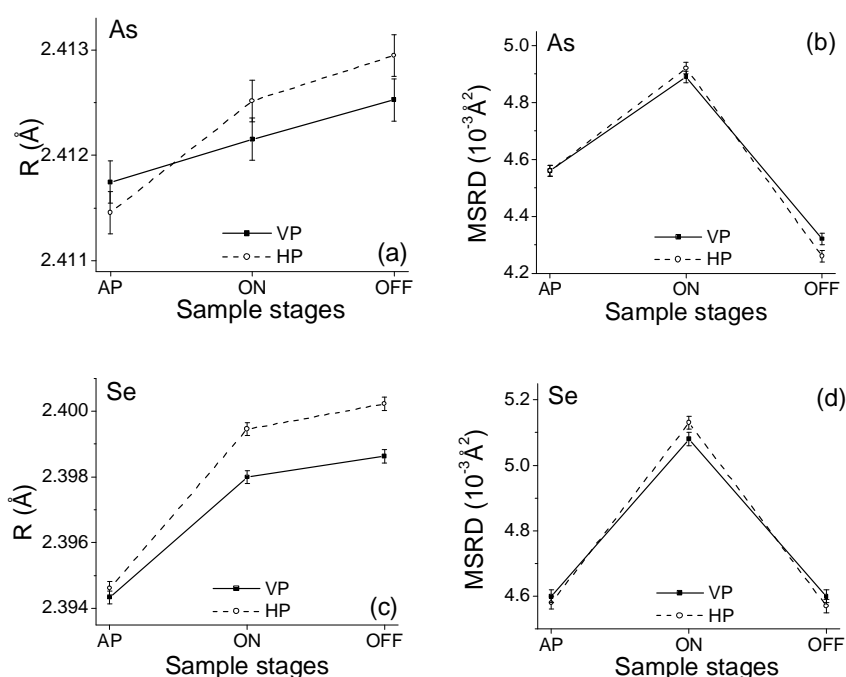


Fig. 9. The change in average nearest-neighbor bond distance (R) and the disorder (mean square relative displacement, MSRD) for As and Se atoms in amorphous $\text{As}_{40}\text{Se}_{60}$ when an as-prepared (AP) sample is exposed to polarized laser light (ON), and after the light is turned off (OFF). The polarization of the laser light is either parallel (HP) or perpendicular (VP) to that of the X-ray probe beam [67].

PAD in elemental Se should be simpler to understand, but it was investigated by EXAFS subsequently due to the need of experiments at low temperatures ($T_g \sim \text{RT}$) [61-63]. To observe any temporary PAD, which disappears on removal of light, the experiment must be conducted with in situ laser irradiation. Another major advantage of in situ experiment is that the relative error is considerably reduced, since the experimental conditions remain nearly fixed, except for the presence or absence of the light beam. Kolobov et al. [62] conducted first such EXAFS experiment on selenium at 15-300 K, which was irradiated in situ by white light. Fig. 8 shows how the normalized coordination number (CN) and the disorder parameter (mean square relative displacement, MSRD) change when as-prepared (stage 1) Se films are irradiated at 30 K with light on (stage 2), with light off (stage 3), and finally after annealing at 300 K (stage 4). No change was detected in the bond length under these conditions. The average CN for Se was determined to be 2.2 implying that, in comparison to crystalline Se, about 20% atoms are in three-fold coordination from inter-chain bonding. Exposure

to light further adds to the inter-chain coordination and to the disorder by bond alternation. Removal of light restores the coordination environment to pre-irradiation condition but the increased disorder persists until the sample is annealed near T_g . The initial increase in CN and MRSD has been interpreted as an indication of photomelting [64]. The in situ EXAFS observations on As_2Se_3 provide additional insight with regard to how PAD of a triply coordinated As may differ from that of a doubly coordinated chalcogen atom [65]. In this work, the most significant change was observed in the disorder around Se, which increases on exposure to light, but mostly recovers when the light is removed. There was no detectable change in the structure around As. Since this was a stoichiometric glass, there must be wrong Se-Se bonds preexisting in the glass, which were preferentially affected by the light as predicted by theoretical simulations [66].

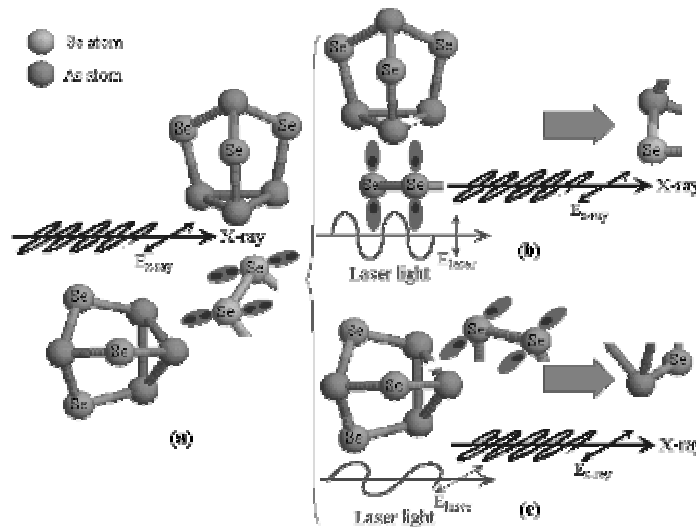


Fig. 10. Schematic of the polarization dependent structural changes in an $As_{50}Se_{50}$ film. (a) The starting film is inhomogeneous consisting of As-rich (As_4Se_3) and Se-rich regions in as-prepared films. (b) Vertically polarized laser light breaks $As-As$ bonds, and excites and reorients the lone pairs of Se atoms to form vertical $As-Se$ bonds. (c) Horizontally polarized laser light breaks $As-As$ bonds, and excites and reorients the lone pairs of Se atoms to form horizontal $As-Se$ bonds [67].

For a direct observation of polarization dependent PAD, the scope of in situ EXAFS experiment has been expanded by exploiting the fact that X-rays in a synchrotron are polarized with E parallel to the ground [67]. Thus EXAFS data have been obtained on As-Se glassy films with in situ exposure by bandgap light of polarization either parallel or perpendicular to that of the X-rays. Fig. 9 shows that on average the nearest-neighbor distance, R , from the Se atoms increases as the sample is illuminated. This expansion of structure is permanent as the value of R remains about the same when the light is turned off. The variation of R for As atoms parallels the expansion around Se. The combined increase of R for both the elements provides an atomistic explanation for the photo-expansion observed in these materials [2].

The difference between the data for Se atoms under two polarizations is a striking feature of Fig. 9. It is the first atomistic observation of a light-induced vector expansion in any glass, indicating anisotropic expansion of the local structure. It means a polarization-dependent driving force for mass transport from illuminated region to the unirradiated region such as observed by Salimonia et al. [45]. A microscopic mechanism of PAD in $a-As_{50}Se_{50}$ is proposed from these measurements: The absorption of bandgap light promotes electrons to low-lying unoccupied conduction-band (antibonding) states, which can cause bond breaking [11,66,68]. The *permanent* photostructural changes are associated particularly with the excess $As-As$ bonds (such as in As_4Se_3 clusters). The absorption of light preferentially breaks such highly strained $As-As$ bonds (present in a triangular configuration in the As_4Se_3 molecule), resulting in the formation of heteropolar $As-Se$ bonds with

excess Se atoms in the glassy matrix. As a consequence, the structural disorder around As decreases (not shown). This bond breaking and reformation occurs in random orientations, so that there is little light-polarization dependence of the change in disorder around As atoms. By contrast, the structural flexibility of the Se atoms allows easy bond reorientation so that the newly formed As-Se bonds are along the **E** field of the laser light (see Fig. 10). From X-ray absorption near-edge structure (XANES) for As in As_2S_3 with in situ irradiation, Lee et al. [69] have suggested that after photo-excitation AsS_3 structural units align preferentially with respect to **E**. The transformation of homopolar bonds (As-As and Se-Se) to heteropolar bonds by light excitation is energetically preferred. Such a reaction is expected to increase the average nearest-neighbor distance of Se atoms and decrease that of As atoms, as observed.

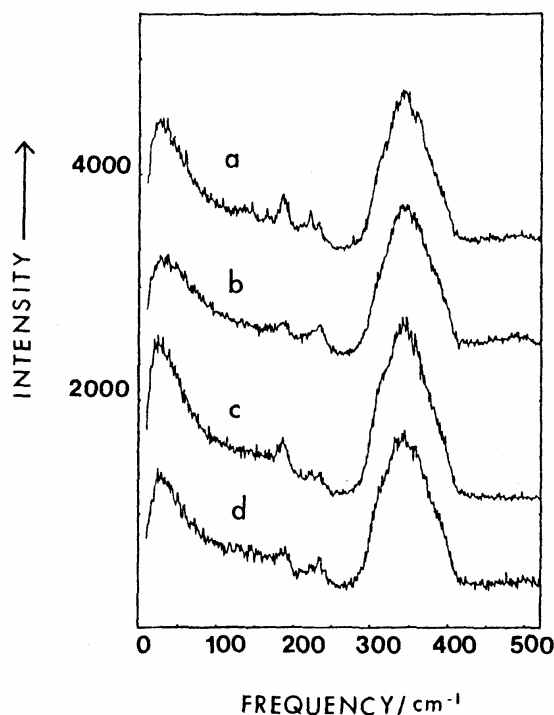


Fig. 11. Raman spectra of As_2S_3 film indicating the reversibility of photoinduced structural changes between exposures to bandgap light and annealing. (a) initial annealed state, (b) after photodarkening by Ar laser light, (c) second annealed state, and (d) after photodarkening for the second time. Reprinted with permission from [70]. © Taylor and Francis (1984), <http://www.tandf.co.uk/journals>.

The results of Raman spectroscopy essentially confirm the observations of EXAFS, and provide additional insight about the mechanism of PAD. It has been used for identifying the structural changes due to irradiation, but the magnitude and identification of specific PAD is generally difficult to determine [63,70-76]. Useful information related to PAD has been obtained in terms of the changes in bond configuration. For example, photoinduced changes in Raman spectra have helped understand the nature of permanent and reversible PAD: The starting sample of an amorphous As-S glass may consist of As_4S_4 and S_2 fragments with homopolar As-As and S-S bonds [74,76]. These bonds react to form a polymerized As_2S_3 glass structure consisting of more stable As-S bonds when the sample is illuminated or thermally annealed the first time. On the other hand, in a well-annealed sample, exposure to light (of a higher frequency) may lead to the opposite reaction:



Fig. 11 shows the reversibility of this reaction, where the peak at 231 cm^{-1} represents As-As bonds. Thus the Raman data have provided convincing evidence that PAD involves bond breaking by

bandgap irradiation of As_2S_3 [70,77]. Besides the changes in nearest neighbor environment, photoinduced modification has been observed in the medium range structure in the form of polarization dependent rearrangement of mesoscopic fragments [73]. The PAD of a given atom from such changes is probably too small to be detected by a direct technique like EXAFS.

3. Photoinduced atom displacement in polymers

The polymers are usually soft materials and, therefore, are likely to exhibit PAD and corresponding changes in properties relatively easily. The underlying process is very similar to what happens in glasses: the light creates a photoinduced excited state in which the charge is redistributed. As a result, there is new polarization in the structure, which then induces specific atomic displacements. Photoplastic recording is a simple illustration of the latter step, where the photoinduced modulation of charges across a polymer creates plastic deformation [78]. Due to the poor stability of polymers, PAD may lead to not only a change in physical structure but also a change in the chemical structure and composition. Thus one observes photoinduced isomeric reactions where molecular structure is reorganized or, in some cases, photolysis/photosynthesis where new products are formed. Interesting photoinduced isomeric reactions occur primarily in synthetic polymers. They consist of light elements like H, C, N and O, which are difficult to observe directly. Therefore, most of the information about PAD in these polymers is obtained indirectly by spectroscopic methods, which identify variation of structural units rather than the position of individual atoms. By comparison, photolysis/photosynthesis reactions are noted predominantly in natural polymers, often with a transition metal acting as catalyst. Then the movement of metallic element can be observed directly by methods like EXAFS. For example, with in situ irradiation, Chance et al. [79] found a ~ 0.005 nm increase in Fe-C distance as a result of photolysis of carboxymyoglobin at 4 K, and Guiles et al. [80,81] established photoinduced structural rearrangement at the various stages of oxygen evolution in higher plants. The salient features of PAD through isomeric reactions in technologically interesting polymers are summarized next.

3.1 Photoinduced atom displacement in polymers by isomeric reactions

The most interesting form of PAD in polymers is identified in photochromism, which is defined as a reversible photoinduced transformation of a chemical specie between two or more forms having different optical behavior. Often, one may also observe a corresponding change in dielectric constant, chemical reactivity, geometrical structure, viscosity etc. [82,83], which are all related to the PAD in the material. Among polymeric materials, liquid crystals (LC) have inherently anisotropic structure that can be modified by external electrical, optical or mechanical field [84]. Leading examples of photochromic polymers include those based on azobenzene, spiropyrans, fulgides, diarylethenes. Among them, azo polymers have been investigated most extensively [10]. The photoinduced response and PAD behavior of this class of polymers is based on a photoinduced *trans* \leftrightarrow *cis* isomeric transformation, as shown in Fig. 12. Photoexcitation of the lone pair electrons on nitrogen plays an important role for initiating the transformation of the *trans* isomer. The *cis* structure is formed through two different excitation paths involving either the rotation or the inversion about the — N=N — bond. The *trans* form is generally more stable than the *cis* form, so that the forward reaction is induced by UV light, but the reverse reaction can be induced by heat or light of longer wavelength. The properties of the rod-like *trans* (or E) isomer and the bent structure of the *cis* (or Z) isomer can be very different as illustrated by Fig. 13, which compares absorption spectra of the *trans*- and *cis*-(4-butyl-4'-methoxyazobenzene) in n-hexane. Since the absorption spectra for the two forms are significantly different and one form can be converted to the other form by irradiating with light of two different wavelengths, such materials are attractive for rewritable optical memory (without using any heating such as used currently).

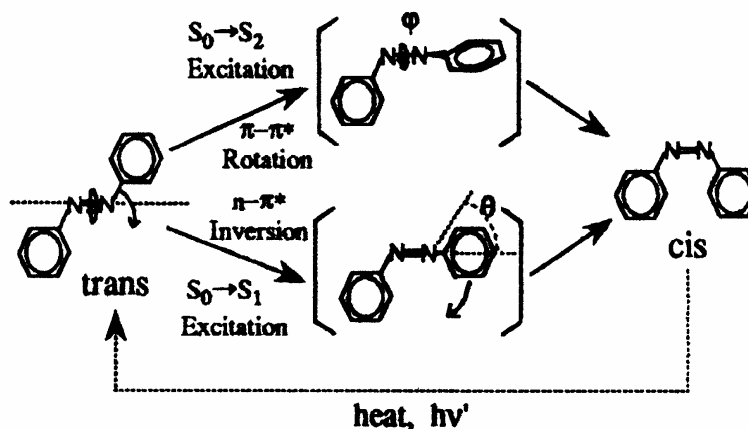


Fig. 12. Photoinduced trans \leftrightarrow cis isomerization reaction of azobenzene chromophore. There are two possible paths for forward reaction, depending on the wavelength of excitation light. The backward reaction can occur by yet another wavelength of by heat [9]. Reprinted with permission from Chemical Reviews. © American Chemical Society (2000).

In many cases, the molecular configuration of the photochromic isomers is so different that if such molecules are added to a non-photochromic matrix, the structure of the latter is affected by the E \rightarrow Z reaction. If the matrix is a liquid crystal, photoinduced isomerism can be used to alter its mesophase structure [3]. Thus the properties of a liquid crystal doped with small concentration of photochromic molecules can be reversibly controlled by appropriate light exposure. This process is termed photoalignment. For example, the nematic to isotropic phase transition of a liquid crystal is triggered by the isomeric reaction of 4-butyl-4'-methoxyazobenzene shown in Fig. 12, and a 100 times amplification is noted in its image recording [85]. Naturally, the net photoinduced change in the properties of such a material is determined by the characteristics of both the active dopants as well as the liquid crystal matrix.

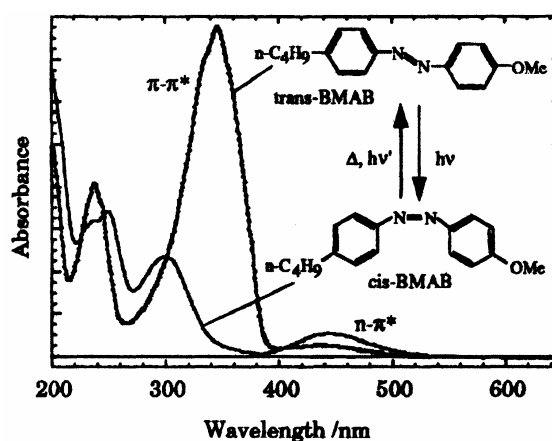


Fig. 13. Photoinduced isomerization can cause significant change in the absorption spectrum of azobenzenes as shown here for the two isomers of [4-butyl-4'-methoxyazobenzene] in hexane [9]. Reprinted with permission from Chemical Reviews. © American Chemical Society (2000).

When a photochromic molecule like azobenzene is exposed to linearly polarized light, the absorption coefficient varies as $\cos^2 \theta$, where θ is the angle between the electric dipole transition moment (approximately parallel to the long molecular axis) and \mathbf{E} vector of the light [86,87]. Thus the product of the isomeric reaction has preferential orientation inasmuch as permitted by the opposing thermal randomization. A polymer containing such photochromic molecules develops photoinduced dichroism, the direction of which can be manipulated by the direction of light polarization. It can be

also removed by heating to T_g . The combined ability of aligning photochromic molecule by polarized light, and then the same molecule forcing the alignment of molecules in liquid crystal offers an extraordinary opportunity to tailor the properties of such a LC guest-host system [88,89,90]. Thus, by a proper choice of the polymer host, one can control the stability of the aligned chromophores and hence the whole structure.

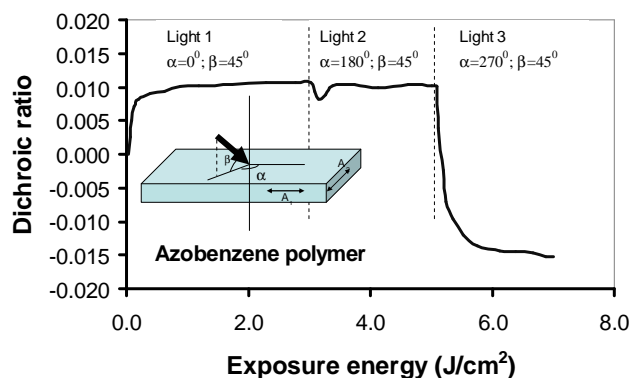


Fig. 14. Creation of photoinduced dichroism in an azobenzene polymer by the slantwise directionality of unpolarized 436 nm laser beam. Dichroic ratio is shown as a function of dose. The film was irradiated first with light-1, and then successively with light-2 and light-3 with different irradiation azimuthal angles as shown in the inset [91].

An interesting consequence of the $\cos^2 \theta$ dependence of the polarization induced alignment is that the light causes no PAD when $\theta = 90^\circ$ i.e. when the transition moment of the chromophore is parallel to the direction of light propagation. In other words, the direction of propagation gives an additional degree of freedom, besides polarization, for controlling the direction of alignment, and it should be possible to align or reorganize the structure in three dimensions with polarized light with variable angle of incidence [91,92]. Alternatively, one may expect alignment of chromophores by the direction of the beam even if it is not polarized. Fig. 14 illustrates the creation of dichroism in poly [2-(4-phenylazo-phenyloxy)ethyl methacrylate] by a 436-nm unpolarized light. The dichroism ratio, $DR = (A_2 - A_1) / (A_2 + A_1)$, correlates with the direction of the beam where A_1 and A_2 are absorbances for the two azimuthal angles.

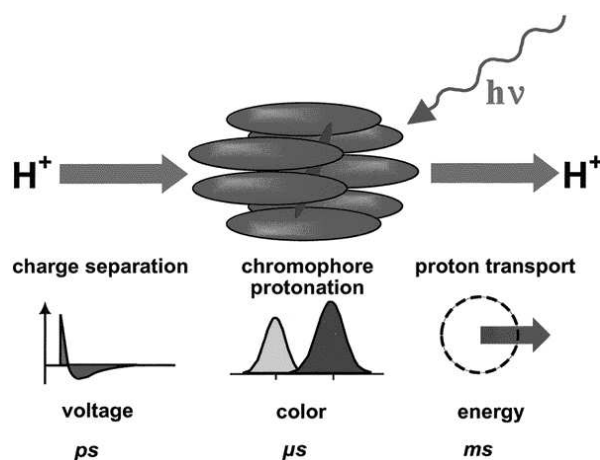


Fig. 15. Schematic representation of the three steps of photoinduced proton transport across the cell wall of BR. Photon absorption causes a charge displacement within ps. Subsequently, with the help of Schiff base the proton moves out, and a change of absorption spectrum is observed [93].

Although most of the technologically important photosensitive polymers are manmade, there are unusual examples of natural proteins that show parallel photochromic behavior and associated PAD. Bacteriorhodopsin (BR) is the model photochromic bio-polymer which, due to its high thermal and chemical stability, has been considered for photonic applications including optical recording, holographic storage, nonlinear filtering, spatial light modulators, phase conjugation, pattern recognition, etc. [93]. It forms the basis of photosynthesis and sustains halobacteria (*H. salinarum*) in high salt, low oxygen environment where chlorophyll synthesis is not possible. The cell wall of the bacteria consists of patches of purple membrane (PM) made of BR as two dimensional crystallites. A key step in this complex energy conversion and photocycle process is the reversible transport of proton across the PM, which begins with the photoinduced trans \rightarrow cis isomeric transformation of a C=C bond within the BR [94-96]. It acts as a proton pump transferring up to 100 protons per second out of the cell and across the membrane, creating electrochemical potential gradient as a means of energy storage. The PAD of protons is a complex process involving several intermediate structures and steps. Overall, the exposure of BR to light excites electron across the bandgap into a Frank-Condon excited state, with large shift in electron density, which in turn modifies Schiff base group connecting the seven helices of BR and induces proton transfer out of the cell [93,95]. Fig. 15 shows a schematic of this multi-step PAD of protons from left to right in BR across the membrane that consists of BR helices. The three basic events and their time scales are shown at the bottom.

4. Concluding remarks

Visible and UV light can cause PAD in inorganic glasses as well as in polymers, and one may observe similar photoinduced scalar and vector phenomena in both classes of materials such as a change in color or volume, enhancement of diffusion, creation of optical anisotropy, etc. In both cases, photons excite electrons and the charge distribution of the excited state leads to PAD, even to the extent of bond-breaking. Often the starting material is isotropic and homogeneous, yet the PAD can be anisotropic, depending on the direction of beam propagation and/or polarization. If the sample consists of anisotropic molecular units (which may be randomly oriented), an unpolarized light beam can create anisotropic PAD.

In general, the magnitude of PAD in glasses is much smaller than that in polymers. This difference in photo-response cannot be just due to the difference in the primary bonding of the atom that is being excited. There is enough evidence that strong covalent or covalent-ionic bonds are broken in both cases so that in the initial stage the presence of weak van der Waals bonds (which exist only in polymers) cannot be significant. Hence, the large PAD in polymers has to be due to the ease with which the structure conforms subsequently. At this stage, the flexibility of the network (chains in polymers, or 1/2/3 dimensional network of glass), especially the flexibility of the local structure around the excited atom is crucial to PAD, which should be considered in designing new materials. In general, a chain structure would be more flexible and able to transfer excitation potential to longer distances than a three-dimensional structure. However, when local flexibility is not known, overall flexibility, which is nominally linked to the shear strength, annealing point, or the glass transition temperature, can provide useful guidance.

Finally, we note that notwithstanding the commonality of PAD in glasses and polymers, there appears to be a lack of communication between the researchers of these two fields. There is little indication in the literature that one community has benefited from what is well known in the other community. For example, the concepts of chromophores and isomerism have been greatly advanced and exploited by the polymer community, but not discussed much by the glass community. Likewise, the idea that the PAD of a particular atom can trigger and control the properties of another molecular unit is confined just to the study of polymers. Thus, cross-disciplinary interactions can be highly beneficial for the application of PAD in devices. Purely from the much larger effort on polymers, one might expect the glass community to benefit more at this stage. Overall, polymers exhibit larger PAD but the effect is not sufficiently stable. On the other hand, glasses have greater thermal and chemical stability, but show relatively small PAD. So, for optimum properties, novel glass-polymer (i.e. inorganic-organic) materials may be developed, which would combine their advantages on molecular scale.

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