Физика и техника полупроводников, 1998, том 32, № 8

Towards understanding the photo-induced changes in chalcogenide glasses

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(Получена 16 февраля 1998 г. Принята к печати 23 февраля 1998 г.)

The various irreversible and reversible photo-induced phenomena in chalcogenide glasses, among these isotropic as well as anisotropic effects, were considered up to now to have different origins. Upon reexamination, we find that the elemental photostructural steps are the same for all these phenomena. These are non-radiative recombinations via transient excitons yielding changes in local bonding configurations. The anisotropic changes arise from geminate recombinations of electron-hole pairs which fail to diffuse out of the microvolume in which they were excited. A unified explanation of the large variety of photo-induced changes is presented.

1. Introduction

Academician B.T. Kolomiets and his great school of scientists laid the groundwork to the study of the large and fascinating family of materials known as chalcogenide glasses. Perhaps the most interesting phenomena exhibited by these glasses are the light-induced changes of their properties. Nearly 30 years ago, reversible and irreversible photostructural changes in a variety of physico-chemical properties were discovered [1] and soon thereafter, by Kolomiets and his collaborators [2], the photo-induced optical anisotropies. These discoveries were followed by the observation of irreversible giant photo-contraction [3] of freshly deposited films of these materials, of photo-induced crystallization [4] as well as amorphization [5], of photodoping by metals [6], and more recently by the astonishing findings of photo-induced fluidity [7] and an anisotropic optomechanical effect [8]. These phenomena result from illumination with bandgap light or subgap light of the Urbach absorption region at both ambient and low temperatures [9].

Indeed, this is a surprising variety of photo-induced phenomena and the time for discovery of new ones might not yet be over. It would be most unsatisfactory if one had to search for a different origin and microscopic mechanism for each one of these effects. This has been the tendency recently. For example, it has been stated [10,11] that there is a fundamental difference between centers in the chalcogenide glasses that yield photo-induced anisotropies on the one hand and photodarkening on the other, which is one of the reversible photostructural changes. Moreover, most of the literature makes a clear distinction of the origins of reversible and irreversible photostructural changes [12]. Any model which is based on specific centers [6,11,13–16] such as valence alternation defects [17] can obviously not explain large morphological changes such as photo-induced fluidity [7], photopolymerization [18,19], the giant photo-expansion [20] and contraction [3] or the new reversible anisotropic optomechanical effect [8], because the number of these defects never exceeds a small fraction of one percent of the constituent atoms [15,21].

It is the aim of this contribution to explore the possibility that there is one type of microscopic mechanism which leads to the different photo-induced effects.

Since the first step shared by all these phenomena is the photo-excitation of an electron-hole pair and its recombination, we discuss this in the following section. We then examine various photo-induced effects and see how they might originate from the recombination events.

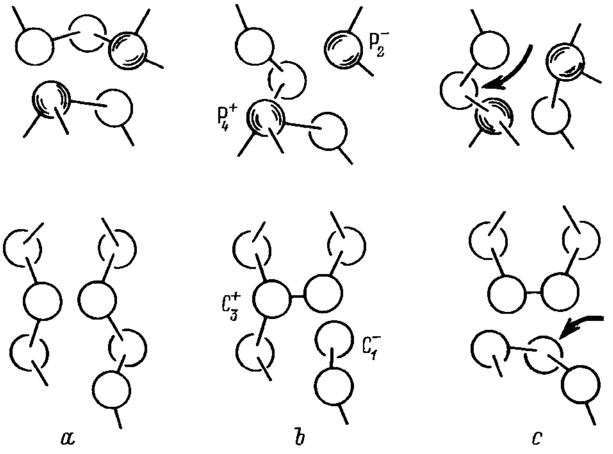
2. Recombination

Chalcogenide glasses have a low photoluminescence efficiency. This suggests, as Street pointed out [22], that these materials provide a non-radiative recombination channel which allows the dissipation of the rather large recombination energy. This recombination is via a transient exciton which can be visualized as a transient intimate valence alternation defect pair [17,23]. The local deformation associated with its formation and subsequent annihilation is the anharmonic energy dissipation process.

Of primary interest for our discussion of photo-induced changes is the fact that the local bonding configuration after recombination and before photo-excitation need not be the same [9,24]. An elementary step of photostructural change can occur. Examples of such elementary steps are illustrated in Figure where (*a*) depicts the local structure before photo-excitation, (*b*) the transient exciton or transient intimate valence alternation pair (IVAP) state and (*c*) the structure after recombination. One notices that atoms can move over atomic distances during such an elementary step.

The change in covalent coordination associated with a change in the local charge or valence state which is the basis for the valence-alternation model subsumes that the charges are quite localized. Indeed, such localization seems to be a general feature of amorphous and vitreous semiconductors. Even photocarriers excited into extended band states localize quickly into band tail states before recombining. Chalcogenide glasses moreover favor structural changes because of the steric freedom of their low coordination atoms [25].

Which optical excitation can result in an elementary photostructural step? Certainly bandgap and Urbach tail



Examples of elementary steps of photostructural changes. White balls are chalcogens (C) and shaded balls are pnictide atoms (P). *a* — initial bonding configuration, *b* — transient self-trapped exciton after photon excitation, *c* — one of several new bonding configurations after recombination with motion of atom indicated by arrow.

excitations, but also excitations between band states and charged valence alternation defect states as well as an electronic excitation, i. e. an electron transfer, within an IVAP. In the latter case, the transient exciton consists of two neutral valence alternation defects which can relax to an IVAP of different configuration than the original one [11,15].

3. Photo-induced fluidity

The illuminated chalcogenide glass will flow under uniaxial stress [7] since local band changes and atomic motions which tend to decrease the local strain energy will be favored [26]. The macroscopic nature of photo-induced fluidity proves that essentially all atoms are involved in these recombination-induced local bonding changes and not only specific and relatively rare defects or structures. In view of the recently discovered anisotropic optomechanical effect [8] one would predict that the photo-induced fluidity is larger for light polarized along the uniaxial stress than for perpendicular polarization.

It is useful to visualize the illuminated state of the glass as a dynamic state with constantly occurring changes in local bonding and atomic motions [24]. These will foster phase separation [27] and phase changes [4,5]. This internal activity will stop when the light is turned off, and the frozen-in structure may relax over time depending on the temperature.

4. Giant densification and photopolymerization

Films which are strongly voided or have columnar structure are obtained with oblique vapor depositions onto cool substrates [3]. Such films can have up to 20% lower density. This density deficit can largely be removed by prolonged illumination [3]. Moreover, vapor deposition of binary and ternary chalcogenide films contain bond-saturated molecular units that exist in the depositing vapor, such as As_4 and As_4S_3. The degree of molecularity greatly diminishes with exposure to light and the films polymerize and resermble more the structure of a bulk glass [18,19].

Both these major topological and structural changes induced by light require motion of atoms and bonding rearrangements. These can result from the cumulative effect of a large number of elementary steps of photostructural changes caused by recombination events [24]. In other words, the dynamic illuminated state will bring about structural changes until a quasi-equilibrium is reached. This so-called light-saturated state is still a dynamic state during illumination because local changes still occur without, however, changing the macroscopic properties. Since thermal annealing will also densify and polymerize freshly deposited films, it is easy to understand that this happens during illumination in the dynamic state [24]. These photostructural changes are, of course, irreversible.

5. Reversible isotropic changes

One of many examples, but a typical one, is the reversible shift of the optical absorption edge [1,9,12,29–32]. Illumination produces a redshift of the edge which increases the absorpsion. This photodarkening can be reversed by thermal annealing near the glass transition temperature. Annealing actually starts after turning off the light and progresses with a wide spectrum of anneal energies.

During illumination, we have the dynamic state with all the recombination-induced local bonding changes and atom motions. The macroscopic physico-chemical properties will change until a balance is reached between thermal annealing, light-induced annealing and light- induced creation of higher energy local bonding arrangements. This balance is called the light-saturated state which depends on light intensity and ambient temperature [24]. It is a state of higher energy relative to the annealed state because, otherwise, it would not return to the annealed state. Its structure differs from that of the annealed state. Diffraction experiments [1,28,29] and computer modeling have taught us that the light-saturated state has less medium range order [32], i. e. is more disordered, than the annealed state. Photodarkening is believed to arise from enhanced ⟨lone pair⟩–⟨lone pair⟩ interactions which broaden the valence band and, thus, cause a redshift of the absorption edge [1,9,28,33].

We see that the microscopic processes driving the reversible and irreversible photostructural changes are the same [24]. The difference arises from the initial states. Only the annealed state can be recovered by annealing, but not the voided and molecular structures of freshly deposited films. Both the reversible and the irreversible changes move toward the light-saturates state. They might not reach it when hindered by topological obstacles which cannot be overcome by the elementary photostructural steps.

The light-saturated state differs in a number of ways from the annealed state. Besides the decrease in medium range order, there is a larger concentration of IVAP defects and of wrong bonds. However, these play, at most, a minor role in the numerous physico-chemical changes associated with the reversible photostructural changes. This is supported by Tanaka et al.'s [34] observation that the efficiency of photodarkening is essentially the same for bandgap and subgap Urbach tail light, but is essentially zero for light absorbed in the defect band.

6. Photo-induced anisotropies

Optically isotropic materials such as chalcogenide glasses can become optically anisotropic because they consist of and contain entities which are optically anisotropic [35,36]. The original macroscopic isotropy originates from the random orientations of the microscopic anisotropic entities. Because of their transverse nature, electromagnetic waves are anisotropic. Therefore, light-induced structural changes will inevitably produce macroscopic anisotropies not only of the optical or dielectric tensor [35–37], but of other physico-chemical properties. For practical purposes, experiments are carried out with linearly or circularly polarized light. The resultant anisotropies are reversible if the photo-structural changes are reversible.

A recombination event which leads to a structural change of a microscopic anisotropic entity will change the orientation or nature of this anisotropy. This constantly happens everywhere in the material during illumination without, however, producing necessarily a macroscopic anisotropy. For this to happen, it is necessary that the recombining electron-hole pair was excited in the same microscopic anisotropic entity which undergoes the structural change. This means essentially that macroscopic anisotropies result from geminate recombinations of electron-hole pairs which do not diffuse out of the microscopic entity in which they were created by absorbed photons [35,36]. The lack of electron-hole pair diffusion and the geminate nature distinguishes the recombination events leading to anisotropies from all the other events which yield isotropic (or scalar) photo-induced changes. This important difference is the cause for the fact that the dependencies on temperature, light intensity, photon energy among other parameters are different for the anisotropic (vectoral) and isotropic (scalar) photo-induced effects.

What are these microscopic optically anisotropic entities in chalcogenide glasses? Intimate valence alternation pair defects (IVAPs) have a dipole moment and form one kind of such entities. After a photo-structural bonding change, its dipole moment will be changed. However, IVAPs are not the only anisotropic entities. Optical excitations from the valence band to the conduction band are transitions from lone-pair electron states to antibonding states [33]. These transitions are polarization dependent because of the low covalent coordination of chalcogens. Hence, any tiny microvolume of the material is optically anisotropic and is altered with a photostructural change. Hence, all optical transitions, i. e. interband, Urbach tail, and defect transitions, are polarization dependent. Each elemental step of photosructural charge alters the local anisotropy. However, a macroscopic anisotropy can result only from non-radiative recombinations of electron-hole pairs that have not diffused away. Which of the various optical excitations fulfills this requirement can be determined by measuring the quantum efficiency for a given anisotropic effect as a function of photon energy.

These arguments can clearly be extended to anisotropies involving circularly polarized light because the small coordination number of chalcogenide glasses provides a local structure with sizable helicity [35,36].

7. Anisotropic optomechanical effect

Krecmer et al. [8] discovered a reversible anisotropic volume change induced by polarized light in a thin film of $As_{50}Se_{50}$. Contraction occurs along the direction of the electric field vector and dilatation perpendicular to that direction. Light from a He–Ne-laser was used whose energy $h\nu \sim 2\,\mathrm{eV}$ falls into the Urbach absorption region. This experiment shows that the anisotropies produced extend to other material properties besides the optical tensor. The magnitude of the effect suggests that the anisotropic microvolumes of the whole material are involved and not only IVAP defects. This is also the interpretation of the authors [8]. These new results imply that the elastic properties, sound propagation and probably many other material parameters of chalcogenide glasses become anisotropic with light exposure.

8. Photo-induced dichroism and birefringence

These phemomena were discovered by B.T. Kolomiets and his school in 1979 [2]. The sign of the anisotropies of the absorption coefficient and refractive index agrees with the prediction of the model which attributes the change to a photostructural change in anisotropic entities or microvolumes resulting in a decrease of oscillator strength for the chosen light polarization and an increase for the other polarization directions [35,36].

There exists disagreement of whether the anisotropic entities are microvolumes of the inherently anisotropic local bonding structures of the chalcogenide material [9,35,36] or whether they are IVAP defects [11,13–15,38,39]. Both may, of couse, contribute with their relative contributions depending on the exciting photon energy as explained in Section 6. With light in the defect absorption band below the Urbach absorption region, only IVAPs can be excited. Larger photon energies can produce changes in the whole material. In the optomechanical experiment discussed in the previous section, the authors detected photo-induced dichroism originating from the anisotropic local bonding structures which are present throughout the material.

In earlier experiments on dichroism, Lyubin et al. [10] emphasized that the effect observed was the same at the beginning and at the end of photostructural changes that lead to photodarkening. This suggests that IVAP centers, whose concentration increases with light exposure [21], contributed negligibly in those experiments. More recently, it was found that the kinetics of the photo-induced anisotropies change with light exposure [15,36]. The observed change in kinetics is no proof that IVAPs are involved. On the contraty, one would expect a much larger change in the magnitude of the anisotropies than observed when the IVAP concentration increases by orders of magnitude. As discussed in Section 5, essentially all local bonding structures change as the material goes from the annealed to the light-saturated state. This is accompanied with a change in density, elastic constants, hardness, and other properties. Therefore, a change in kinetics of the photo-induced anisotropies is not surprising. Moreover, more light is absorbed as the material photodarkens with time which affects the kinetics.

The anisotropic matrix elements governing optical excitations within a microvolume or an IVAP defect region will depend on the photon energy. Therefore, if the photon energy of the probe light differs greatly from that of the exciting light, it is possible that the photo-induced anisotropy disappears at a certain energy of the probe light or reverses its sign. While dichroism depends on the anisotropic absorption coefficient at the photon energy of the probe, the refractive index which governs birefringence is a Kramers–Kronig weighted average of excitations over all energies larger than the probe energy. The reflectivity near the bandgap energy is solely governed by the refractive energy. The reflectivity near the bandgap energy is solely governed by the refractive index while the extinction coefficient need be considered only at relatively high photon energies. A more complete picture of the physical processes would require measuring the induced anisotropy of the complex dielectric tensor as a function of photon energy.

Even in the light-saturated state, the optical axis of the induced anisotropy can be reoriented at will by changing the polarization direction of the exciting light. That illustrates the dynamic nature of the light-saturated state discussed in Section 5. This state is a dynamic equilibrium between constantly occurring local bonding changes during illumination and local thermal relaxation processes [36].

9. Photo-induced anisotropies in light scattering

Many experiments studying photo-induced anisotropies are conducted by sending a laser beam of inducing polarized light through the sample and measuring with a polarized probe beam of greatly reduced intensity the transmitted light intensity and its polarization. Inhomogeneities and density fluctuations will cause scattering which, in addition to absorption, decrease the transmitted light intensity [40]. Scattering can be measured separately in directions away from the beam axis [41].

Inhomogeneities are self-enhancing as localities, which photodarken, absorb more photons from the inducing beam and darken further. The increase in refractive index associated with photodarkening produces light scattering inhomogeneities. With polarized inducing light all these phenomena carry isotropic as well as anisotropic components. The scattered light in turn produces photo-induced changes and inhomogeneities while passing through the material. Concurrently, the inducing light beam experiences self-focusing due to the increased refractive index caused by photodarkening in the laser beam channel. It is clear, therefore, that the rates of recombination events change with time and location even when the intensity of the inducing light remains constant.

These complex and interrelated processes may explain why one observes such a variety of interesting and often puzzling phenomena in these experiments.

10. Discussion

While trying to find a unifying explanation of the photo-induced changes in chalcogenide glasses, we should address particular observations which stood in the way of such a unifying picture. The overemphasis of defects, in particular of IVAPs, as the origin of reversible photo-induced isotropic and anisotropic effects isolated major structural changes such as photo-induced fluidity, the optomechanical anisotropy, and the irreversible photostructural changes into a separate categori. Defects which number much less than one percent of the atomic sites can obviously not account for such major changes. We now understand that any atomic site of low coordination can participate in photo-induced changes which makes the distinction between major and minor effects unnecessary.

Still, in the terminology of defects, it was pointed out that the centers responsible for the optical anisotropies must be essentially different in origin from those responsible for isotropic effects, in particular for photodarkening [11]. As reasons for this conclusion were given (i) the different kinetics, (ii) different spectral excitation dependence, (iii) different annealing temperature and (iv) the observation that photo-induced anisotropies are observed even in glass compositions that show no or hardly any photodarkening.

As was discussed earlier, the main difference between scalar and vectoral effects is that the latter result only from geminate recombinations of electron-hole pairs which fail to diffuse out of the absorption microvolume. It is conceivable that certain defects favor this subset of recombination events. This, however, is not generally the case since the vectoral optical effect is coupled with the optomechanical effect of Section 7 which essentially involves the majority of atomic sites and not specific defects. The different spectral excitation dependence is explained by the special conditions imposed on the subset of recombinations which are able to remember the polarization of the absorbed photon as discussed in Section 6.

The kinetics of the two groups of effects is naturally different. When photodarkening has saturated (zero kinetics) in the light-saturated state, the optical axis of the photo-induced anisotropy can still be reoriented becouse photostructural changes are continually happening in the dynamic balance of the light-saturated state. The local bonding orientations and thus the oscillator strengths are changed preferentially in accordance with the inducing light polarization. This process in turn saturates when it becomes energetically unfavorable to continue.

The elemental photostructural step is the same for both the isotropic and anisotropic effects. The manifestations are different however. Photodarkening results from the cumulative effect of many photostructural steps which decrease the medium range order and increase the lone-pair interactions and, thereby, the width of the valence band. It seems that such major photostructural change requires a higher anneal temperature than the local bonding configuration changes required for optical anisotropies.

Some chalcogenide glass compositions might not exhibit photodarkening because they might not develop a pronounced medium range order in their relaxed annealed state and, hence, might not experience any appreciable increase in the lone-pair interactions in the light-saturated state. These same glasses will nevertheless show photo-induced optical anisotropies due to changes in local bonding structure.

11. Summary and conclusions

Great strades have been made toward understanding the photo-induced changes in chalcogenide glasses. Most, if not all, of them are caused by elemental steps of photostructural change resulting from non-radiative recombination events via transient excitons. These elemental steps occur essentially everywhere in the material where there is freedom from steric hindrance.

Different manifestations of photo-induced changes result when the initial structural states or conditions of the material are different. Reversible changes occur from the annealed state while irreversibility necessarily results when the initial structural state of the material is of higher energy than the annealed state as is the case for voided and molecular films which are vapor deposited. Both the reversible and irreversible changes move toward the structure of a light-saturated state which has less medium-range order and is of higher energy than the annealed state.

During illumination, the material is in a dynamic state which leads at high intensities to photo-induced fluidity, diffusion and phase changes.

Among the many recombination events, there are some which remember the polarization of the absorbed light. These are geminate recombinations occurring in the microvolume of the absorption process. This subset of non-radiative recombination processes yields photo-induced anisotropies of physico-chemical properties. They occur even for unpolarized light because of the transverse nature of electromagnetic waves but are more conveniently observed with polarized light. Since the probability of recombinations falling into this special subset depends on light intensity, temperature, photon energy, and material properties, one finds behavioral differences between isotropic and anisotropic photo-induced changes depending of these parameters.

Among the photo-induced anisotropies are those of the optical properties such as dichroism, birefringence and light scattering among others. They are sometimes difficult to determine quantitatively because the changing optical properties change in turn locally the intensity and direction of the inducing light. This complicated set of problems where the light producing changes at one location depend on changes in optical properties which occurred previously at other locations is inherent to studies of optical properties changed by light. At present, there is no reason to believe that the observed phenomena result from anything different than the changes in transition matrix elements which result from the local bonding changes occurring in all the elemental steps of photostructural changes.

12. Acknowledgments

I am most grateful to Stan Ovshinsky for many enlightening discussions and to B.T. Kolomiets for his warm hospitality during my three visits to his laboratory in 1968, 1975 and 1988.

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