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STRUCTURAL FEATURES AND MECHANISM OF REVERSIBLE PHOTOINDUCED TRANSFORMATIONS IN AMORPHOUS CHALCOGENIDES

dedicated to Stanford R. Ovshinsky on the occasion of his 80th anniversary

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The structural configurations that govern the behavior of the amorphous chalcogenides under excitation are the nano-scale, disordered, layer-like clusters. The competition between breaking, formation and switching of bonds at the cluster boundaries, accompanied by precipitation-dissolution phenomena, gives rise to fractal morphology of these clusters and to the reversible scalar photo-structural effects. The photoinduced anisotropy phenomena are explained in the frame of a model with stimulation of chiral elements induced by polarized light in the disordered layers of the clusters.

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1. Introduction

The effects induced by light in non-crystalline chalcogenides are of high interest both from fundamental and practical points of view. Nevertheless, the structural basis of these effects is poorly understood in spite of the numerous papers published till now [1].

The discovery of reversible change in the optical absorption of amorphous As_2S_3 was reported in the early 1970's [2] and a consensus is now reached that the origin of the effect is the modification of the structure as shown by the reversible change in the X-ray diffraction pattern [3].

In spite of the great variety of models proposed for reversible photo-structural transformations no consensus have been reached up to now, and this is due to the difficulty to observe directly the local atomic structure transformations by traditional methods. The reversible photoinduced changes are weak as they embrace less than 10 % of the atomic node concentration.

This paper try to shed more light on the structural aspects and mechanism of reversible scalar and vectoral photo-induced transformations, in the frame of an unified point of view.

2. The structural problems of the arsenic chalcogenides

In liquid As-Se Coulet et al. [4] have shown that a miscibility gap exists. A phase separation was discussed. Clusters are usual in liquids. Two types of clusters are possible: closed and open. The clusters in liquid arsenic chalcogenides (As-Ch) seem to be mainly based on disordered quasi-planar layers [5]. The disordered layers are quasi-free (mobiles) and, therefore, a stacking is possible. This structural feature can explain why the first sharp diffraction peak (FSDP) in the X-ray diffraction pattern of liquid As-Ch is abnormally high. When the liquid is quenched, the quasi-layers become more rigid, and their packing more constrained. As a consequence, the FSDP, intensity and width decreases [6].

The structural features of the liquid seem to be, at least partially, retained in the glassy or amorphous state. When the non-crystalline As-Ch glasses are subjected to high-pressure (as e.g. in a-As_2S_3) [7] the FSDP vanishes. In this case the basic layers become more distorted, while the free space between them disappears, and, as a consequence, the layer stacking is less evidenced.

In solid arsenic chalcogenides the structure seems to be biphasic [8]. A sub-phase of layered clusters and a disordered sub-phase, with small, closed or open molecular fragments represent the phase configuration. The average extent of the ordered sub-phase (in fact the thickness of the layer stacks) is supposed to be around 2 nm, according to the half-width of the FSDP [9]. This corresponds to 3-4 layers in a cluster.

Every disordered layer in arsenic-chalcogenides is characterised by atomic asymmetry similar to the case of crystal. Taylor et al. [10] have shown by NMR measurements on ^{75}As, that arsenic sites in As_2S_3 (As_2Se_3) crystals are similar with those in non-crystalline materials and that the outrigger rafts hypothesis of Phillips [11] seems to be not valid. In fact the vibrations of the edge-shared tetrahedral-like configurations, as shown by Elliott [12] can explain the companion Raman peak, attributed by Phillips to outrigger rafts. On the other hand, Tanaka and Nakayama [13] demonstrated the electronic similarity that must reflect the structural similarity in amorphous and crystalline chalcogenide semiconductors.

Popescu and Bradaczek [14] suggested the paracrystalline structure in amorphous materials, under the form of reminiscent crystal-like configurations that account for the medium-range order in non-crystalline chalcogenides.

Pfeiffer, Paessler and Lee [15] tried to demonstrate, by modelling experiments, that the general structure of As-Ch glasses is characterised by chiral elements of the type -As-Ch-As-Ch-. This means that the disordered layers are built from such chains, with some bonding between them.

An other feature of the elementary disordered layer is the presence of wrong or homopolar bonds (As-As, Ch-Ch). The difference in energy between homopolar and heteropolar bonds in binary arsenic chalcogenides is small and, therefore, the homopolar bonds are in equilibrium with the heteropolar ones. The homopolar bonds are in higher amount than dangling bonds, as shown by Tanaka [16].

3. Mechanism of photo-induced transformations

Liu and Taylor [17] have shown that the action of light on amorphous As-Ch is a complex process: a rapid component that induces a disordered structure and a slow component, that produces a sort of annealing. The faster process involves a rapid increase in defect population until the population of pre-existing defects is reached. The slower process seems to be related to a change in the amorphous matrix.

Many scientists have discussed what type of transformations is induced by light. Because the light of band gap energy is the most efficient for photoinduced phenomena, it seems that bond breaking is implied [18]. Likholit et al. [19] were the first to show that a rupture of covalent interatomic bonds (As-S, As-Se) is responsible for the photoinduced change in the scalar properties of amorphous chalcogenides.

Recently, Kolobov [20] has suggested that both homopolar and heteropolar bonds can be broken. If this is the case, then we are dealing with two competitive processes bond destruction and bond formation. The problem is: what are the consequences of these processes? Because the most probable sites of the action of light quanta are situated on the border of the structural clusters, it is reasonable to suppose that the release of free chalcogen is possible.

There exist many indications that the light with band gap energy acts especially on the lone pair electrons of chalcogens [21]. Non-bonding p-electrons are absolutely necessary for photo-induced phenomena. As early as 1974, Ovshinsky and Sapru [22] have shown that lone-pair electrons play a key role in the transition between bi-stable configurations possible by photo-excitation. As a consequence of photo-excitation a dissociation of chalcogen from the As-Ch bonds is possible.

Popescu et al. [23] have shown that exposure with band gap illumination leads to some release of sulfur from the $Ge_xAs_{40-x}S_{60}$ films. Owen, Firth and Ewen [24] have shown that absorption of the photons of energy greater than band gap light, when produced, generates a hole-electron pair. If the opposite charges are sufficiently separated, a broken bond will result. The dissociation of the arsenic-chalcogen bond is followed by thermal diffusion of the arsenic to form arsenic clusters. This photodecomposition is manifested optically as a photo-darkening phenomenon.

In other paper Popescu et al. [25] have shown that when the above band gap irradiation is made in air, a thin As_2O_3 layer is formed at the surface of the a-AsSe films. In the same type of films, Krishnaswami, Jain and Miller [26] have shown that during irradiation in ambient atmosphere by sub-band gap light one obtains the enrichment of the film surface with oxygen and selenium. When the films were illuminated in vacuum no change in the electronic structure of the chalcogenide material was detected by XPS.

At dawn of the research in photo-induced phenomena, Berkes et al. [2] clearly evidenced the photodecomposition processes in As_2S_3 and As_2Se_3, occurred under band gap light excitation. The clustering of arsenic atoms can be, subsequently, produced by the association of atoms, which have been partially dissociated from the original network. Upon heating, the arsenic precipitate from the two-phase aggregate would go back into solution. Later, Keneman, Bordagna and Zemel [27] have interpreted the photodarkening (PD) in As_2S_3 films irradiated by light with band gap energy, as due to arsenic cluster formation. From Raman scattering studies Frumar, Firth and Owen [28] have concluded that a number of As-As bonds were created by light in As_2S_3 glass. The formation of wrong bonds was confirmed by EXAFS [29].

Frumar et al. [30] have shown that under light exposure the photolytic reactions in As-S films are more important at room and lower temperatures, while the reactions among fragments As_4S_4 and S_n do not play a role. In fact, in stabilised (annealed) films the molecular As_4S_4 and sulfur chains are in low amount, and in thermodynamical equilibrium with the open layer-like clusters.

It is interesting to remark the case of a parented oxide glass: Sb_2O_3-$SbPO_4$. Nalin et al. [31] have shown that PD is due to defect centres originated by a change of the oxidation number of antimony. The light induces a breaking of Sb-O bonds in the glassy network. The mean co-ordination number of Sb decreases by irradiation. The structure is completely restored after heating near T_g.

Last but not least we must point out that the photographic process in classical white-black photography is based on the decomposition of silver halides (e.g. BrAg) and the release of silver. When the dispersion of the BrAg phase is higher (i.e. the particle size decreases), the chemical activity of BrAg is enhanced and the sensitivity to light increases.

According to the experimental facts, a scenario for the photodarkening (PD) and photobleaching (PB) processes is suggested:

During illumination the light quanta excite the LP electrons on chalcogen and change the chalcogen equilibrium position or even break its bond with arsenic or with other sulfur atom. It appears a competition between destruction on the border and building on the account of the surrounding medium (molecular As-Ch or Ch_n small clusters). Thus, the disordered quasi-layers are transformed step by step. They can grow, reduce statistically their size or change the structural order (disorder) according to the dominance of one or another process. The formation of charged defects induced by light leads to the layer repelling and slip motion of the stacked layers, as shown by Shimakawa in his model [32]. Recently, Tanaka [33] has questioned the existence of charged defects in chalcogenide glasses and has shown that wrong bond amount is estimated at ~1 at.% and this concentration is much greater than that of the charged defects.

On the other hand, some homopolar bonds are formed by photo-transformation of the open clusters. Then the quasi-layer becomes wavy and this corresponds to an average thickness higher than for the case of absence of the homopolar bonds. A more disordered layer is characterised by a larger mean thickness, as shown by Popescu on the case of an amorphous arsenic model [34]. Therefore a volume expansion is produced due to the inflation of the layers.

By asking the experiment, Tanaka [35] has shown that during PD in As-Ch films the clusters grow in thickness while the interlayer quasi-distance increases. The photo-induced volume expansion (PVE) evidenced in amorphous arsenic chalcogenides receive, thus, a straightforward explanation.

The development of the disordered layers is a random process. The photo-transformation of the open clusters is due to the competition creation-destruction. As a consequence fractal clusters are produced. The growth of fractal clusters was, recently, simulated [36]. In a simple simulation with one step relaxation on the cluster margins one gets branched clusters with fractal dimension 1.74. When more relaxation (in the second and third vicinity of the initial binding position of a chalcogen unit) is permitted, then the clusters become more round, and the correlation length of the fractal decreases.

The simulation of the fractal objects, when applied to the growth and transformations of the disordered chalcogenide layers, is of high importance because recently Meherun-Nessa et al. [37] have shown that the fundamental optical absorption in amorphous chalcogenides can be interpreted by introducing the density-of-states on fractals.

The second stage, characteristic to the light action, corresponds to the slow component, which "anneals" the material, and this means that more homopolar bonds are transformed into heteropolar ones. This determines a diminishing of the volume expansion effect. The concurrence of the first stage effect of light (with homopolar bonds formation) and second stage effect (with the destruction of the homopolar bonds) explains why in some glassy compositions one observes a PVE phenomenon while in other type of glasses one observes a photoinduced volume contraction (PVC).

In arsenic chalcogenides photo-bleaching is produced either by annealing or by irradiation with light of different intensity compared to that used for PD. Igo and Toyoshima [38] investigated the As-Se-S-Ge system and have shown that PD is produced with weak light while PB is produced by illumination with intense light that causes annealing. For As_3Se_2 films high intensity light causes PD. If, after PD the films are irradiated by low intensity light, then PB do appear [39]. This fact illustrates the importance of the pre-irradiation for the scalar photo-induced phenomena.

During PB the photo-structural modifications are opposite. By annealing some bonds are again broken and rebuilt. Simultaneously the chalcogen diffuses deep into layers and breaks the small arsenic clusters formed during light irradiation. The overall modification is determined by the competition between bond changes and chalcogen diffusion (from the disordered sub-phase) with the formation of new bonds. The original structure is then more or less restored. It is interesting to remark that during photo-crystallisation, firstly an intermediary amorphous state does appear and then the released heat transform this state into a crystalline one. This fact proves that an advanced PD with dominance of the creation processes (the intermediary state) followed finally by a rapid transformation of the defect layer into a crystalline one, is produced, as shown by Matsuda [40] for $GeSe_2$ films.

High stresses in the distorted (defected) layers trigger the local bonding switching, and, by a co-operative effect, the crystalline configuration is reached. In our opinion, the very intense light gives rise firstly to PD, followed by PB, and finally to crystallisation.

It must be pointed out that some experiments have evidenced that films and glassy powders with high amount of defects are more sensitive to light than polished plates of the same composition [41].

In our scenario for photoinduced phenomena the defects and impurities play the role of catalytic sites for the light action. The defect probability is highest for the composition with comparable amount of arsenic and chalcogen (Ch). That is why PD increases with arsenic concentration, and the maximum is situated at As_3S_2 [42].

A puzzling fact is the opposite behaviour of Ge-Ch glasses compared to As-Ch glasses: the film thickness decreases and band gap increases during illumination of Ge-Ch films, while the film thickness increases and band gap decreases during illumination of As-Ch films [43]. Annealing determines a reverse effect in both systems.

The opposite behaviour of Ge-Ch films, compared to As-Ch ones, can be explained by the easy change of co-ordination of Ge and Se atoms, due to the tendency to form cubic rock salt structure typical for crystalline GeSe. During annealing of a GeSe amorphous film the structure shifts towards a more crystalline one: i.e. germanium changes the co-ordination from 4 to 3, while selenium changes the co-ordination from 2 to 3. By illumination the reverse modification is stimulated [44]. Because the three-valent germanium implies an electronic transfer of $1e^-$ from Se to Ge, then some repelling between quasi-layers is produced and, thus the swelling effect (evidenced by the increase of the film thickness) during annealing can be simply explained.

As concerning the PD (PB) effects in amorphous chalcogen (S, Se), the bond breaking dominance during illumination and bond (re)formation during annealing seems to be a reasonably explanation in the frame of the model with competitive processes. After bond breaking, the VAP states can be created spontaneously because small atomic shifts after bond breaking are finally followed by reinsertion of end of chain atoms in the network of quasi-random packed chalcogen chains. The bond breaking and/or bond formation are followed by structural rearrangement at not too large a scale. This scenario agrees with the experimental results and is not in contradiction with the explanation given by Kolobov [45], which has shown that the photo-induced VAPs can be regarded as a kind of seeds around which a structural change takes place causing the photodarkening.

4. Mechanism of photo-induced anisotropy

The photo-induced anisotropy (linear dichroism, linear birefringence) and also photoinduced gyrotropy (circular dichroism, circular birefringence, optical activity) excited by linearly polarised light or circularly polarised light have been observed in thin films and in bulk chalcogenide glasses. The first observation of induced anisotropy by linearly polarised light was made by Zhdanov et al. [46, 47].

Recently new effects have been discovered: polarisation-dependent photo-doping [48], polarisation-dependent photo-crystallisation [49] and polarisation-dependent optomechanical effect [50] (see also [51]).

The photo-anisotropic effects, or vectoral effects, are induced by illumination with band gap or sub-band gap light [52]. The light with higher energy is less efficient. This is opposite to the case of scalar photoinduced effects (PD, PB). Lyubin and Tikhomirov [53] have found that the induced anisotropy and the reversible PD (and photorefraction) are independent processes.

From the effect of reorientation of the anisotropy when the polarization direction of the inducing light is switched, it follows immediately that electrical dipoles which respond to the changing direction of the electric field vector must be at the origin of the anisotropy. The most obvious candidates after Adriaenssens, Tikhomirov and Elliott [54], to provide the dipole moment are the charged defects, D+ and D^-, of the standard negative -U model for chalcogenide glasses. The fact that the ground states of those defects would be located just below the conduction band, respectively, just above the valence band, explains the maximum sensitivity of observed photoinduced phenomena to sub-band gap illumination. A macroscopic anisotropic structure can be formed in the glass with the presumed orientation of IVAP lone pairs being orthogonal to the electric vector of the inducing light. The IVAPs are native dipoles D^+D^- or $C^{3+}C^{1-}$ where D or C is a chalcogen atom.

This explanation is different from the first explanation of the PA phenomena given by Zhdanov et al. [46,47], according to which the macroscopic anisotropy is produced by the reorientation of specific structural configurations in the sulphur chalcogenides. These configurations were supposed to be crystalline As_2S_3. It is our opinion that this mechanism does not work due to steric hindrance during the local spatial movement. Only a large co-operative phenomenon could be effective.

The opposite changes of photo-induced anisotropy of transmittance and scattering lead Lyubin and Klebanov [55] to suppose that the creation of anisotropically scattering centres is the basis of the whole group of photo-induced vectoral phenomena in amorphous chalcogenides. The excitation of the anisotropy by sub-band gap light can be, thus, understood. The energy of light quanta is not sufficient to break the covalent bonds, but is enough to produce some changes in the system of weak (Van der Waals) bonds or to change the dihedral angles betwen bonds.

The scenario for the photo-induced anisotropy is most probably related to the chirality properties of the chalcogenide material. The ordered chirality is a property of the crystalline analogues of chalcogenide and oxide glasses (e.g. spirals in c-As_2Se_3 or As_2S_3, or right- and left-hand modifications of c-SiO_2 [56]. The optical activity is not related essentially to the spiral ordering of the atoms, but is related to the spiral ordering of the electrical polarity, because this has as a consequence a convenient deformation of the polarization ellipsoid. The rotation of the polarization plane of the light wave is independent on the crystal orientation, and is proportional to the length travelled by light ray in the crystal [57].

The anisotropy is induced as follows: absorption of light causes a "flipping” of two-fold coordinated selenium in helical sites so that a degree of local chirality is produced as supposed by Elliott [58]. The polarised light induces a specific arrangement in the -As-Ch-As- chains with the favouring of the staggered positions of the covalent atoms by relieving the dihedral angle distortions (these positions are most favourable from the energetic point of view). Such modifications of chalcogen positions at small scale can be realised without spatial hindrance and without long-range reordering of the structural configurations. The competitive processes of bond breaking, switching and formation are helping for the chiral rearrangement of the chalcogen atoms.

The above explanation of the photoinduced anisotropies does not disagree with the views of Tanaka and Ishida [59], which have shown that photo-induced anisotropy, is caused by photo-electronically oriented crystalline growth. The orientation and growth correspond to the position of the clustered layers perpendicular to the electric field of the polarised light wave.

A surprising finding was that the light induced re-orientation or erasure of anisotropy is not associated with any change in the scalar photodarkening [60], or, even, is anti-correlated [61]. It seems that light interacts predominantly with the domains oriented in the direction parallel to the electric vector of the exciting light [62] and the overall anisotropy is the resultant of the co-operative action of the microscopically anisotropic domains. Kolobov et al. [63] demonstrated that not only defects but also main covalent bonds are re-oriented due to excitation with linearly polarised light. In the frame of the model with chiral induced orientation of the covalent bonds in the -Ch-As-Ch-As- chains, the induction of anisotropy and its stimulation when pre-irradiation with non-polarised light is made, can find a satisfactory explanation. The pre-irradiation simply brings the As-Ch layered clusters nearer to the crystalline-like configurations, and from this state the chiral orientation of the bonds is easier to produce. The observation made by Fritzsche that some anisotropy can be acquired in amorphous arsenic-chalcogenides even by non-polarised light (it is interesting to observe that in this case the anisotropy characteristics depend on the position of the light spot on the glass sample!) gives strong support to the chiral model of photo-induced anisotropy. The light induces a partial ordering in the open clusters, that become more crystalline, and therefore, some optical activity can be produced, due to chiral chains in the basical structural units.

5. Discussion and conclusions

The mechanism of PD and its dependence on the light intensity can be explained as being related to the modification of the order and morphology including the size change of the layered fragments. The PD is due to the increase of the disorder and appearance of new homopolar bonds, including separation of small arsenic clusters, while the layer extent decreases. In the same time chalcogen atoms diffuses away in the intercluster disordered sub-phase. The volume of the material increases, i.e. an expansion occurs, as experimentally observed. As opposite, the breaking of the wrong bonds and diffusion of chalcogen and arsenic precipitates within the main ordered sub-phase (made of layered clusters) determine the PB. A more ordered sub-phase with extended crystalline-like configuration is formed. The volume of the material decreases as clusters are contracted due to better layer packing.

The anisotropic properties induced by light is caused by the development of chiral configurations based on -As-Ch-As-Ch-... chains, and similar to those from crystalline chalcogenides. The correctly oriented clusters relative to the polarisation plane of the exciting light (i.e. the quasi-planar layers perpendicular to the electrical vector of the light wave) is more stimulated to change the dihedral angles toward the more favourable chiral configuration of the atoms, and this gives the macroanisotropy effects observed.

The results of the simulation of the complex polymerization-destruction processes show that in the amorphous chalcogenides a structural state based on fractal clusters occurs. The model with competitive creation-destruction-switching processes seems to be able to explain various effects produced in non-crystalline chalcogenides under the influence of light irradiation. The self-assembly of the basical structural units with specific properties is an important feature in the model.

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