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CHALCOGENIDE GLASSES IN OPTICAL RECORDING: RECENT PROGRESS

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A mechanism of reversible photostructural changes is discussed based on recent in-situ experiments. An important role of lone-pair electrons accounts for why this process is unique to chalcogenides. An approach to achieve ultra-high resolution based upon use of Super-REsolution Near-field Structure (Super-RENS) is described.

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1. Introduction

Amorphous chalcogenides, sulphur and selenium being the simplest representatives, are intrinsically metastable and as such can be easily modified by external agents, by light in particular. The first observation of photo-induced changes in chalcogenides was reported by Chang [1] but it were papers by Keneman [2] and Berkes, Ing, and Hillegas [3] that draw the attention of numerous investigators to such changes. It was shown that illumination of amorphous chalcogenides, alternatively and interchangeably called chalcogenide glasses and chalcogenide vitreous semiconductors, resulted in a shift of their absorption edge to lower energies. Annealing at temperatures close to the glass-transition temperature restored the initial optical properties. This phenomenon was referred to as reversible photodarkening [3]. It was soon found that changes in optical properties were accompanied by changes in conductivity, photoconductivity [4, 5], dissolution rate in various solvents [6] etc. The total of these results have led various groups of investigators to a conclusion that the reason behind these changes were changes in the structure. Discovery of reversible changes in x-ray diffraction pattern by Tanaka [7] was direct and unambiguous proof of such changes. To interpret the observed phenomena, several groups came up with the so-called configuration coordinate approach [8, 9]. Within this approach, the ground state of the system possessed a double well adiabatic potential. Optical excitation transfers the system to the higher (metastable) state and thermal annealing returns it to the lower (ground) state via the energy barrier separating the two states.

In most case non-polarised light is used and the induced changes are called scalar. Use of linearly polarized light results in photo-induced anisotropy in initially isotropic glasses [10-14] and the effects induced by polarized light are often called vectoral effects.

While the reversible photostructural changes occur within the amorphous phase, there are other processes (photocrystallisation and photoamorphysation) which change the state of chalcogenides. Under some conditions the structural changes are believed to be caused by an athermal mechanism, in other cases photo-induced heating of chalcogenides plays an important role.

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An important feature of the photo-induced changes in chalcogenides is their ultra-high resolution with the presently experimentally recorded limit on the order of a few nanometers [15].

All the above mentioned processes open up a possibility of application of chalcogenides for optical recording and various attempts to this end have been and are being made, some of them very successful.

It should be noticed that the nanometer scale mechanism of such changes has long remained unclear and it was not until very recently that in-situ structural studies performed on amorphous selenium unveiled the possible nanometer scale mechanism of reversible photostructural changes.

The present paper presents the summary of the authors' recent activities. It first summarises the results of recent in-situ studies of reversible photostructural changes. This is followed by a discussion of the nanometer-scale mechanism of such changes which answers the question why amorphous chalcogenides are unique materials. Discussion of a relationship of the uncovered mechanism with the vectoral effects and photocrystallisation concludes this part of the paper.

The second part of the paper describes a recently suggested technique for super-dense optical recording. We believe that this approach, named Super-Resolution Near-field Structure, or Super-RENS 16, opens up new possibilities for using amorphous chalcogenides in future optical memory devices.

2. Nanometer-scale mechanism of reversible potostructural changes

Most of early studies were performed ex-situ and on binary chalcogenides. As a result, the data analysis was complicated and important information about the structure of the excited state, via which the transformation takes place, was missing. One of the first in-situ experiments was in-situ Extended X-ray Absorption Fine Structure (EXAFS) measurement. Details on the experimental equipment and procedure can be found in [17]. It was found that upon photoexcitation the amplitude of EXAFS oscillations reversibly increased. This is illustrated by Fig. 1 where the Fourier transformed (FT) EXAFS spectra for the film in the ground state and in the photo-excited state are compared. The observed increase in the FT magnitude can be caused by two reasons, viz., a decrease in the disorder parameter and an increase in the coordination number. From a fundamental point of view the former is unlikely since photostructural changes are known to be accompanied by increased disorder.

The curve fitting based in a single scattering theory demonstrated that, indeed, the average coordination number of Se reversibly increases in the photoexcited state by about 5-6 %, i.e. about 10 % of the total number of Se atoms increase their coordination [17].

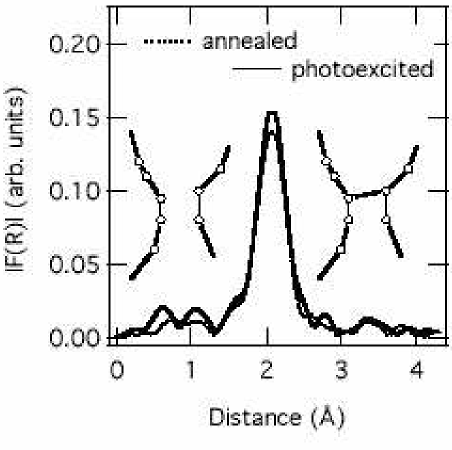

Fig. 1. FT EXAFS spectra of annealed and photoexited a-Se film measured at 30 K. An increase in the peak magnitude is caused by the cross-linking of the neighbouring chains.

The change in the bonding geometry in the photo-excited state was further versified by Raman scattering [18]. Two new features were detected in the spectrum for the photoexcited sample which is an unambiguous evidence for a change in bonding geometry rather than a change in the ordering.

The structural change caused by photoexcittion is illustrated by schematic diagrams in Fig. 1. Light excites a lone-pair (LP) electron transferring it from the non-bonding orbital (the top of the valence band) to the anti-bonding orbital (conduction band), leaving the other LP electron unpaired. Provided the neighbouring chain is close enough and the excited state lives long enough it is energetically favourable to form an interchain bond. This formation of the interchain bond is the initial stage of the photo-induced structural transformation. We would like to stress here two aspects. One is that the majority of defects in liquid chalcognides are argued to be three-fold coordinated defect pairs [19, 20]. This shows a similarity between the liquid state and the photo-excited solid state enabling one to consider the latter as photo-induced melting [21, 22]. The second aspect is an important role of lone-pair electrons in this process which accounts for why the photo-induced changes are primarily observed in chalcogenides.

The formation of the interchain bonds requires atomic movement not only on behalf of the two atoms directly forming the bond but also on behalf of their neighbours. As a result, strain is accumulated and bonds are liable to sever. It should be kept in mind, however, that once formed, the interchain bond is undistinguishable from the intrachain covalent bonds and, as a consequence, *any* of the bonds subtended at the three-fold coordinated atoms can sever in order to release the strain. Provided that the newly formed bond breaks, the initial structure is restored and a certain fraction of bond breaking goes through this pathway. If, on the other hand, bonds which were initially intrachain bonds break, a pair consisting of a three-fold coordinated defect and a dangling bond is formed. Each of the constituent species possesses an unpaired electron and should be ESR-active.

In order to verify the possibility of the latter process, photo-induced ESR experiment have been performed [23-25]. It was found that, indeed, ESR-defects are created in amorphous Se, their concentration reaching the value of 1020 cm^{-3}. It was additionally found that two kinds of defects were created in *equal* quantities which is the first reported proof that the defects are created *in pairs*. One defect has been clearly identified as a dangling bond.

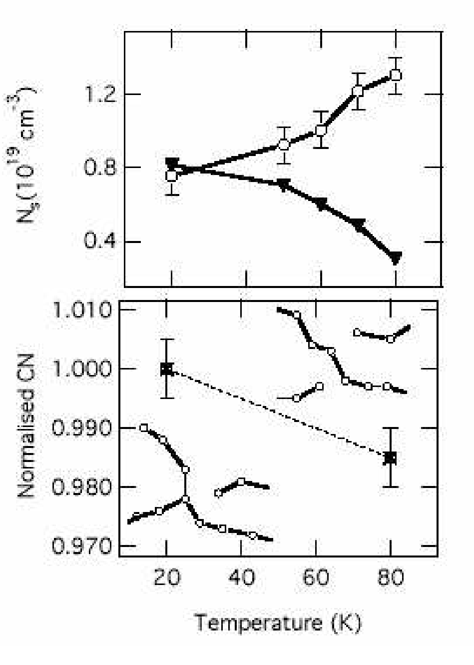

Fig. 2. Complementary temperature dependence of concentration of the two types of photo-induced ESR centres (top) is accompanied by a decrease in the average coordination number (bottom) suggesting that three - fold coordinated defects are decomposed into a normally

bonded atoms and a dangling bond.

Upon annealing, the concentration of defects changes in a rather unusual way. In the temperature range of 20 to 90 K the total concentration of defects remains unchanged but their fractional concentration changes (Fig. 2(top)), i.e. a conversion of one kind of defects into the dangling bonds takes place. A detected change in the average coordination number accompanying this process (Fig. 2(bottom)) suggests that the other kind of defect has higher coordination, i.e. is a three-fold coordinated defect which decays into a normally coordinated atom and a dangling bond.

At a yet higher temperature (90 to 160 K), the ESR signal decreases but the defects do not disappear, they are converted into charged (ESR-inactive) defects. Annealing above 160 K results in partial recovery of the initial structure and at 300 K the recovery is complete. These steps of the process are described in detail in the original papers [25].

The whole process can be present as follows:

$$2C_2^0 \rightarrow 2C_3^0 \rightarrow C_3^0C_1^0 \rightarrow 2C_1^0 \rightarrow C_3^+C_1^- \rightarrow 2C_2^0$$

(subscripts = coordination, superscripts = charge of the defects)

We would like to mention here that *ab initio* simulation of photoexcitation of amorphous selenium [26] gave the results which are in perfect agreement with the experimental conclusions.

Up to now, we were not considering the polarization of the light. If we do include the polarization into consideration, some new aspects come into play. Polarised light interacts predominantly with electrons whose wave functions have a larger component in the direction parallel to the polarization plane of the light. As a result, the formation of the interchain bonds takes place in a pre-determined direction and the newly formed structure is no longer randomly oriented. Such a conversion between non-bonding and bonding electrons depending on the polarization of the light have been detected experimentally for a model chalcogenide glass As_2S_3 [27].

Table 1. Bond length in photoexcited films of crystalline and amorphous Se (results for two consecutive cycles are shown).

Sample	c-Se	a-Se		
		unpolarised light	polarized EX $\perp$ EL	polarized EX $\parallel$ EL
Bond length (± 0.004 Å)	2.37 2.37	2.339 2.341	2.354 2.358	2.357 2.352

Provided the photon density is high enough, the local structural changes correlate and changes on medium-range order scale become possible. Table 1 shows the bond length in a-Se excited by non-polarised and polarized light 28. One can see that the Se-Se bond length is longer in the case of the polarized light excitation. It has to be mentioned here that there are two factors determining the bond length in Se: *intra*chain forces and *inter*chain forces. In crystalline Se, the chains are ordered and both factors are important for the bond length stabilization. In amorphous Se, the interaction between the chains is much weaker and, as a result, intrachain forces dominate making the bond length shorter in the amorphous state. (Se stands out in this respect: in most solids the bond length increases in the amorphous phase). The fact that the bond length is longer in Se irradiated by polarized light indicates that the interchain interaction is increased, i.e. chains are oriented parallel to each other.

Rotation of the polarization plane of the light by 90 degrees, causes a reversible change in the Se K-absorption edge (Fig. 3). Since the dipole selection rules require that the unoccupied states in the K-edge be p-orbitals, the observed change corresponds to a situation when the Se chains are oriented perpendicular to the polarization plane of the light. We believe that this orientation of the chains is a prelude to anisotropic photocrystallisation of Se [29-32].

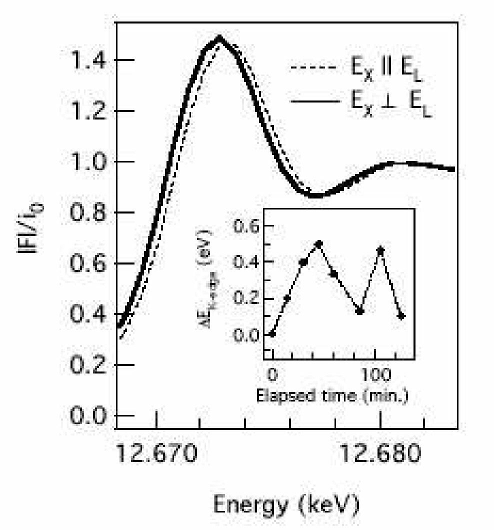

Fig. 3. K-edge XANES spectra of s-Se film irraditated by linearly polarized light with the polarization plane oriented parallel and perpendicular to the polarisation plane of the probing x-ray beam. The insert shows a reversible shift of the edge upon rotation of the polarization plane of the light by 90_.

At this point we would like to turn to photocrystallisation. While the mechanism of this phenomenon is still under debate and may be due to thermal effect of the light, the above electronic mechanism of the bond switching may equally well explain the photo-crystallisation. Indeed, light induces a pair of neutral defects which can diffuse apart until they acquire a charge. At this moment, the Coulomb interaction is switched on and the subsequent stage proceeds depending on the photon density. If the photon density is low, then the distance between the defects originating from the same site is small compared to the distance between the pairs and the defects recombine geminately. If, on the other hand, the photon density is high, the distance between the defects originating from the same site is comparable to the distance between the defect pairs and recombination can take place between the charged defects originating from different pairs. Since the system tends to minimize its energy, the result of such correlated pair recombination results in crystallization.

A reverse phase-change process, namely photo-amorphisaton, is also possible. Thus a thermally crystallized $As_{50}Se_{50}$ film becomes amorphous when exposed to light [33, 34]. The used light intensities and also direct temperature measurements indicate that the process is athermal. Most likely, the reason for the photo-amorphisation is the strain accumulated in the film during the crystallization. Light weakens the bonds and the system relaxes. Under certain conditions it may be energetically favourable for the system to break the strained bonds in the molecular As_4Se_4 crystal and go back to the cross-linked amorphous state. Photoamorphysation in As_2S_3 and Se have also been reported [35, 36].

3. Super-resolution phase-change optical storage

Most processes described in the previous section take place within the amorphous phase. However, use of light may also change the phase state of the system. The examples described in the previous section refer to continuous light excitation. In case of short laser pulses, and hence higher intensities, the role of heating gets more important. It is believed that (relatively) long laser pulses of ìlowî intensity heat a chalcogenide leading to its crystallization. Short and intense pulses, on the other hand, melt the material which is then quenched into the amorphous state. Such photo-induced phase transition, first reported by Ovshinsky [37], became a basis of present-day rewritable optical storage devices, such as CD-RW and DVDs. The materials of choice in these devices are multicomponent chalcogenides, $Ge_2Sb_2Te_5$ (GST) and $Ag_{10}In_4Sb_{58}Te_{28}$ (AIST) being typical examples.

Although such devices are now widely marketed, none of them completely realizes the high-resolution possibilities offered by chalcogenides. One of the reasons for this is that the size of a single bit is diffraction limited. A promising way to overcome this limit is to use optical near-field. Typically, a near-field device consists of a fibre with the tip (i.e. the near-field source) located at a distance of a few nanometers from the material surface, as is the case in widely used scanning near-field optical microscopes (SNOMs). However, for the optical storage applications this way seems to be a dead-end approach since keeping the distance fixed with a high accuracy between the tip of the fibre and a polymer disk rotating at a high speed is very difficult.

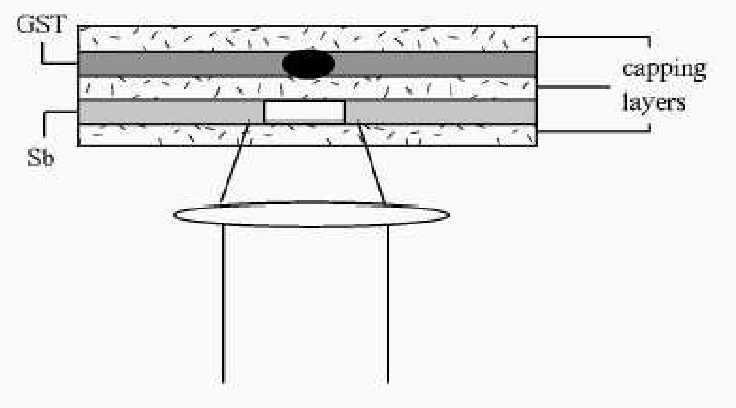

Fig. 4. A schematic presentation of transmission Super-RENS.

A solution to this problem is to incorporate the near-field source into the disk structure. A way to do so is to use a multi-layer structure a typical example of which is shown in Fig. 4. This structure is called a Supper-Resolution Near-field Structure (Super-RENS) [38]. As can be seen from the figure, in addition the GST layer sandwiched between two capping layers there is another layer, Sb in this case, which acts as a masking layer. When a laser pulse hits the structure, the Sb heats up. Since the intensity in the beam has Gaussian distribution, the central part is heated to a higher temperature. When heated, the Sb layer becomes transparent, i.e. an aperture opens in it which serves as a near-field source. The distance between the light source and the recording media is now fixed and determined by the thickness of the capping layer between the masking layer and the GST layer. With optimized parameters for each layer, the aperture in the Sb layer opens for the time sufficient to record a bit into the GST layer. When the disk rotates and the exposed Sb spot moves away from the light, the aperture closes. A similar processes takes place during the read-out stage. This kind of Super-RENS is called transmission Super-RENS and bits with the size considerably below the diffraction limit have been successfully recorded [16, 39].

An alternative design contains an AgO_x layer (instead of the Sb layer). Light causes reversible decomposition of AgO_x and the formation of Ag nanoparticles. Local plasmons excited by light in these particles emit optical near-field. This technical design is usually referred to as scattering type Super-RENS [40]. The latter structure was demonstrated to be a basis for a purely optical photonic transistor [41].

For the efficient information recording, several conditions have to be satisfied. Firstly, the transformations between the amorphous and crystalline states have to be fast in both directions in order to ensure high speed. Secondly, each of the states has to be stable in order to insure reliable storage. As the size if a bit decreases, it is getting more and more difficult to satisfy these requirements.

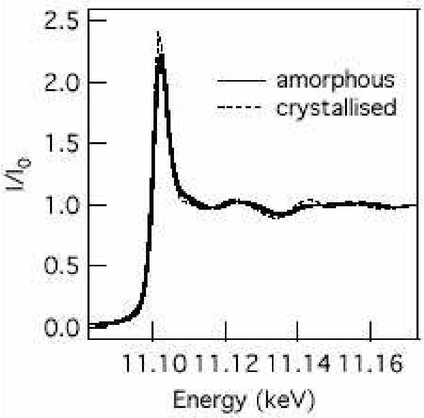

Fig. 5. XANES spectra of amorphous and crystallized GST films.

Although the understanding of crystallisation and amorphisation processes does exist, it is rather phenomenological. In order to be able to perform insightful search for novel materials, it is important to know what exactly bond-switching processes take place at the nanometer scale. As a starting step on this way, we have performed XAFS measurements on amorphous and crystalline GST films. Fig. 5 compares x-ray absorption near-edge spectra (XANES) of the GST film in amorphous and crystalline states. Differences in the region corresponding to the onset of EXAFS oscillations indicate differences in the local atomic structure (more profound than just different disorder). An increased white-line intensity in the crystallized state is an indication of increased density of unoccupied states, i.e. the electronic structure also changes upon crystallization. Proper data analysis is currently underway.

4. Conclusions

Recent in-situ experiments have unveiled to a great degree the nanometer scale mechanism of reversible photostructural changes. It has been shown that the initial step of the process is the formation of dynamic interchain bonds through photo-induced unpairing of lone-pair electrons. The crucial role of lone-pair electrons accounts for why such changes are mainly observed in amorphous chalcogenides. The proposed mechanism also explains the vectoral changes induced by polarized light and correlated structural changed upon excitation with intense light.

A way to overcome the diffraction limit in optical recording through use of Super-RENS has been described and steps to improve its performance have been indicated. This approach is believed to be a prototype of future optical storage devices.

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