Optical and Photonic Glasses

Lecture 29:
Photoinduced Effects in Glasses

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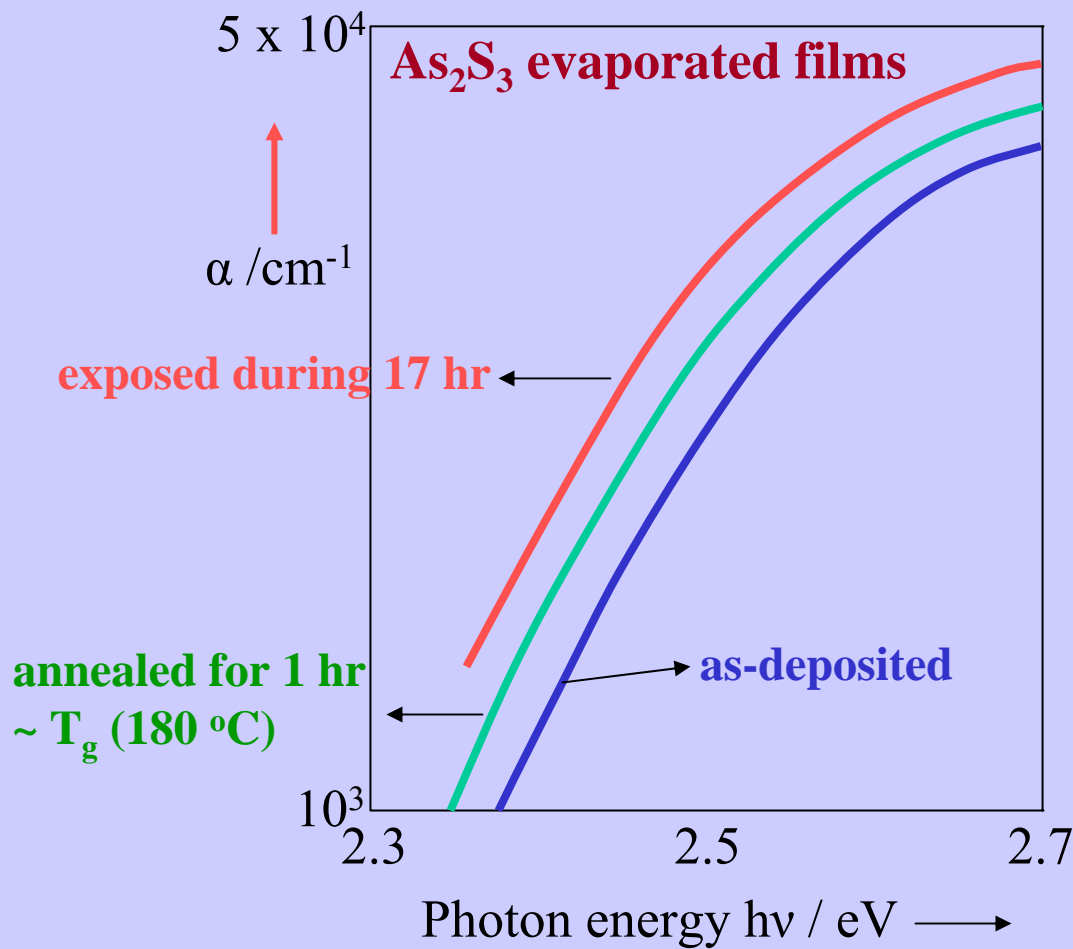**For New Functionality in Glass**

Lehigh University

Photoinduced effects in ChG and other photonic glasses

The following discussion will include photoinduced phenomena like photodarkening and photobleaching, as well as the effects of femtosecond (fs) laser pulses in glass.

Photodarkening (PD) and **photobleaching (PB)**

These phenomena refer to the change in the absorption spectrum of glass by light illumination and are easier to observe in ChG thin films under bandgap light illumination. As shown in the figure, the transmission edge of a As_2S_3 glass film shifts to longer wavelengths upon illumination, corresponding to a *photodarkening* phenomenon.

A variety of photoinduced effects have been observed in ChG, namely photocrystallization, photopolymerization, photodecomposition, photovaporization and photodissolution (of certain metals), all generally accompanied by shifts in the absorption edge, i.e., photodarkening or photobleaching. One of the reasons why ChG's are so susceptible to light-induced changes is the fact that their structures tend to be chain-like or layer-like, rather than 3-D CRN's.

5 x 10^4

As$_2$S$_3$ evaporated films

α /cm^{-1}

exposed during 17 hr ←

(Adapted from: K. Shimakawa et al., Advances in Physics, 1995)

annealed for 1 hr
~ T$_g$ (180 °C) ←

as-deposited →

10^3

2.3   2.5   2.7

Photon energy hν / eV ⟶

Photodarkening: upon illumination to bandgap light during 17 hr, the absorption edge of the as-deposited film red-shifts. Subsequent annealing near T$_g$ leads to some recovery, although incomplete, through photopolymerization. If the annealed film is again illuminated, the exposed state will again be reached. Either PD or PB may be observed, depending on the glass composition and preparation details. Thus, while As-based films usually show PD, Ge-based ones tend to show PB, instead.
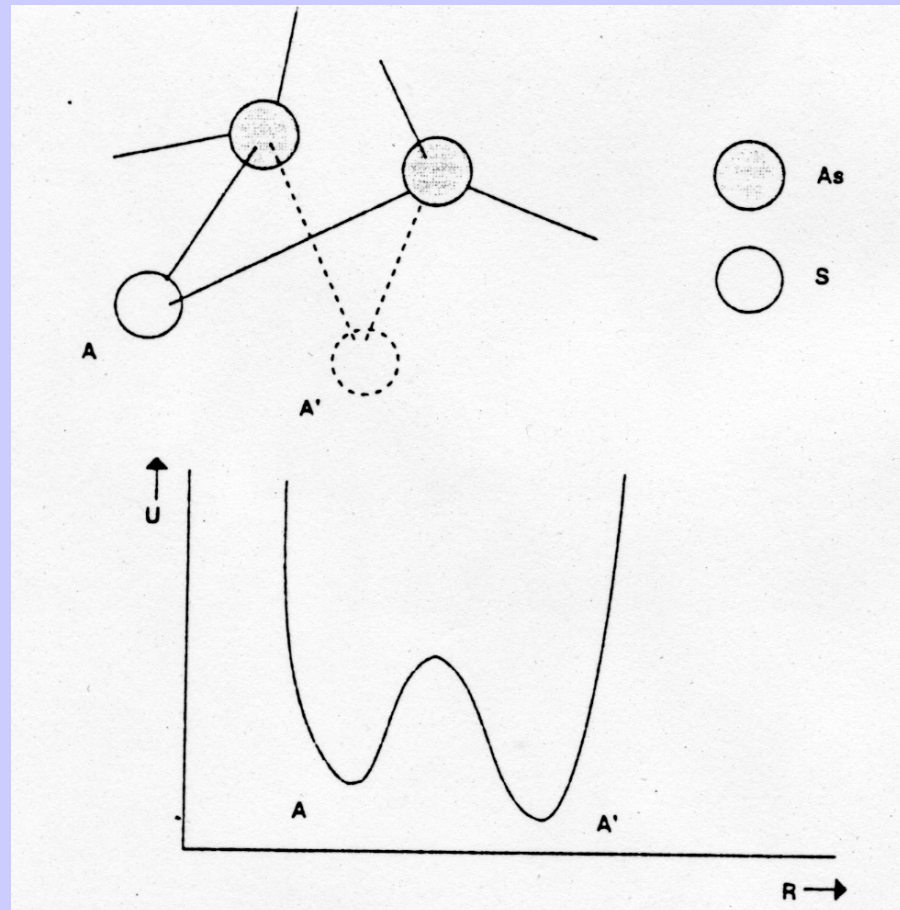
A second reason is that the chalcogen atoms possess non-bonding lone-pair electrons, corresponding to the highest lying levels in the valence band, which are therefore preferentially excited by illumination and thus involved in light-induced reactions to produce structural defects such as 3-fold or singly coordinated chalcogen atoms.

Such effects tend to be *reversible* in well annealed vapor deposited films or in melt quenched glasses. The *irreversible structural* changes, on the other hand, are found mainly in poorly annealed vapor deposited films, whereas *irreversible physicochemical* phenomena occur irrespective of the annealing treatment.

Reversible effects

Reversible photoinduced changes in local atomic structure are induced by photons of energy larger or close to that of the optical gap, E_G and they manifest themselves mainly by small red shifts ($< \sim 0.1$ eV) of the optical absorption edge, i.e., *photodarkening*. These shifts are usually accompanied by small changes in the volume (contraction or expansion). The best example is v-As_2S_3, but similar effcets have also been found in other ChG's like As_2Se_3, GeS_2 and $GeSe_2$. Photodarkening, however, does not occur in c-As_2S_3. Annealing will restore the initial structure and properties.

It has been suggested that the structural changes induced by light consist of minor bond rearrangements involving the chalcogen atoms. A photoinduced increase in interlayer separation has also been suggested.
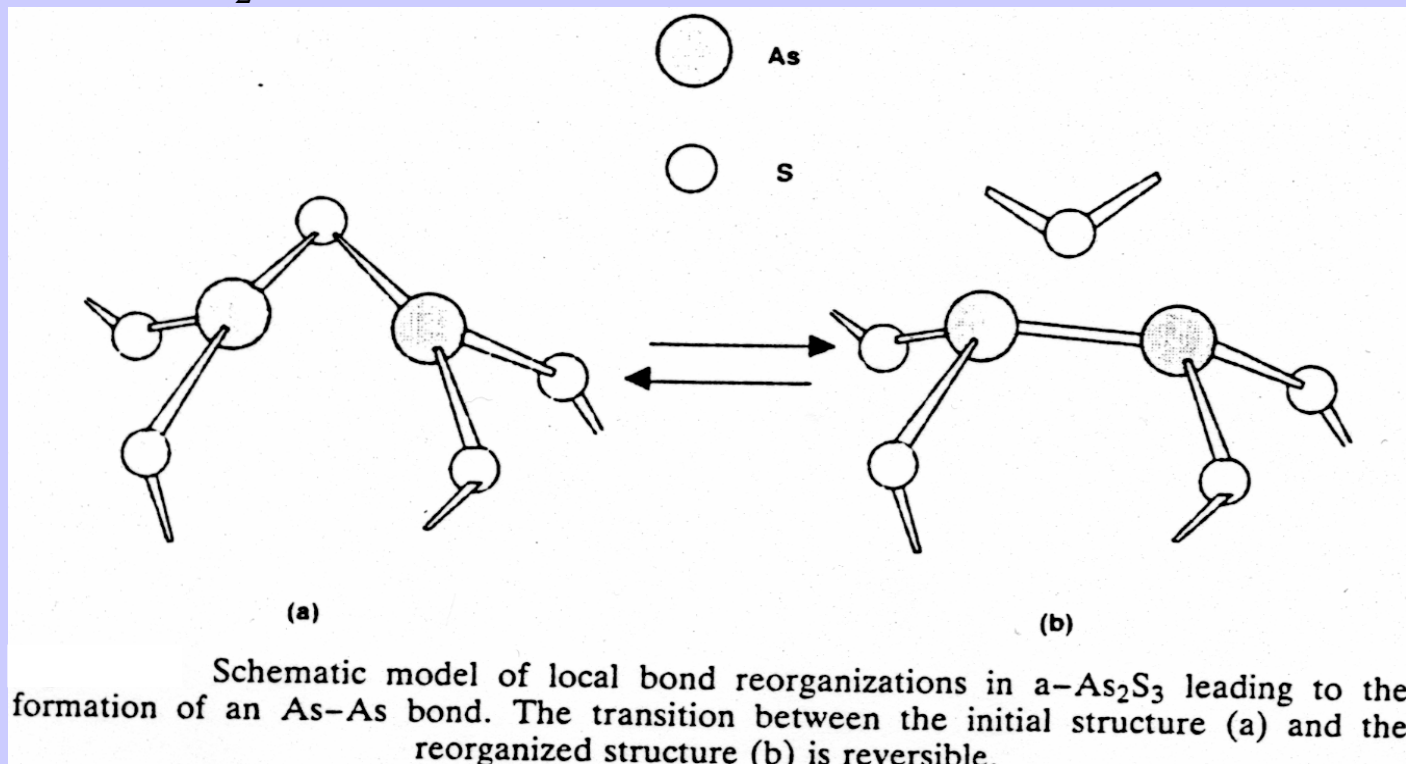

A schematic model of bistable bonding geometries in a−As_2S_3 and the corresponding double-well potential. A and A′ represent atomic configurations before and after illumination, R is some configurational coordinate and U the potential.

(Adapted from: P.J. S. Ewen and A.E. Owen, in, *High performance glasses, Blackie and Son, 1992*)

Photodecomposition

In amorphous As-S and As-Se compositions, when illuminated with photon energies larger than E_G, dissociation of As-chalcogen bonds is promoted, followed by thermal diffusion of As to form highly absorbing metallic clusters, manifested in a red shift of the optical absorption edge, i.e., photodarkening. This photodecomposition is reversible on annealing at T_g.

A local bond reorganization as shown in the figure, without significant diffusion of As, can also give rise to As_2 units, which later revert to the initial state.

Schematic model of local bond reorganizations in a–As_2S_3 leading to the formation of an As–As bond. The transition between the initial structure (a) and the reorganized structure (b) is reversible.

(Adapted from: P.J.S. Owen and A.E. Owen, in, *High-performance glasses*, Blackie and Son, 1992)

Irreversible photo-induced effects

Photocrystallization

Photoinduced crystallization and re-amorphization (requiring the temperature to be first raised to the melting point of the crystals) has been observed in As-Ge-Te films.

Photopolymerization

As-deposited, poorly annealed films of a-As_2S_3, e.g., may contain molecular species like As_4S_4, which were present in the vapor and which, upon illumination, may polymerize and combine with the network. Polymerization causes densification and, with time, the thin films will become identical with melt-quenched glass.

Photoinduced morphological changes

These are changes associated with photocontraction, observed mainly in Ge-Se thin films upon illumination with UV light. Contractions of up to 12% may occur.
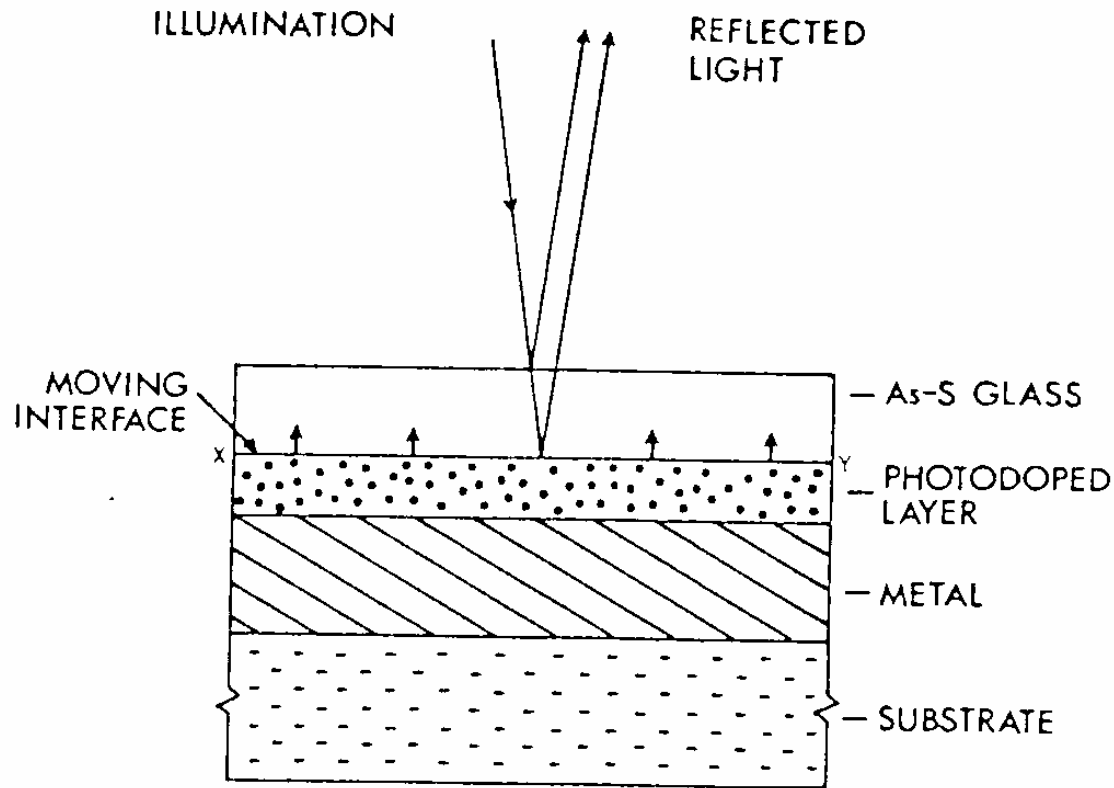
Photovaporization

This has been observed mainly in a-As_2S_3 thin films, at temperatures $> \sim 150$ ºC. It consists of photo-oxidation, followed by thermal evaporation of the volatile oxidation products (arsenic oxide and sulfur).

Photodissolution of metals

This is one of the most useful photoinduced phenomena in terms of applications.

When a chalcogenide glass layer in contact with a metal layer is illuminated, metal ions dissolve into the glass and migrate in the direction of illumination. This is called *photodiffusion*, *photodoping* or *photodissolution* and it is schematically shown in the next figure. The accepted explanation corresponds to a light-induced chemical reaction. The light lowers the energy barrier preventing the reaction to occur at room temperature, so it is expected to be absorbed mostly at the doped-undoped interface X-Y.
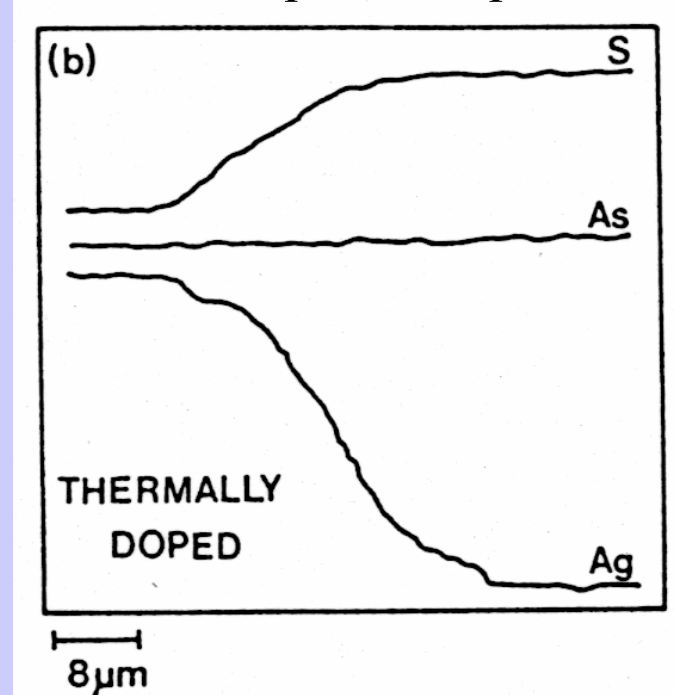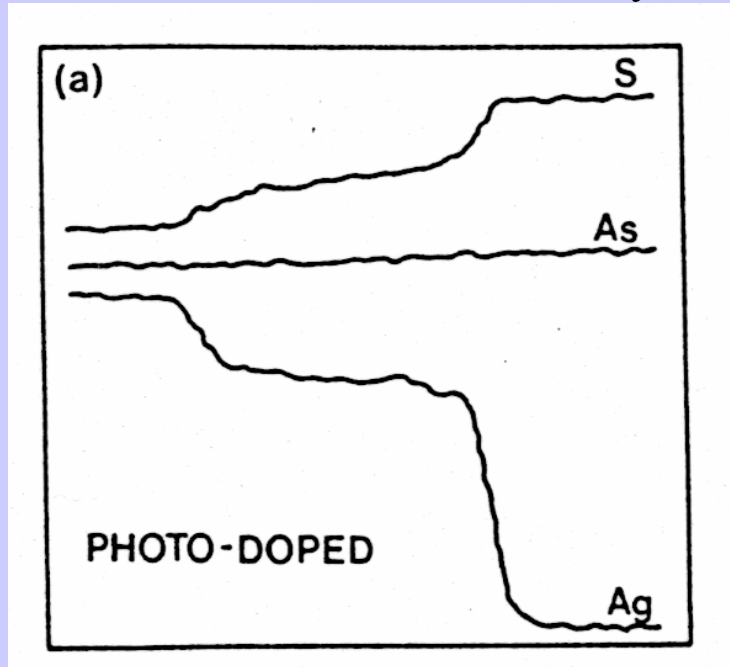
This effect appears to occur in most chalgogenide glasses, whether in the form of unannealed vapor deposited films, well-annealed films, or melt-quenched glasses. Metals like Ag, Cu, Zn, Ag_2S, etc., have been used as the metal ion source, which needs not to be an evaporated film. Up to 30-40 atom% of metal have been introduced into ChG's, to a depth of over 10 μm.

A schematic cross-section through a sample during the photodissolution process. Under illumination, metal ions dissolve into the As–S glass to form a new 'photodoped' material. The photodoped layer continues to grow as long as the sample is illuminated. The light stimulating the process is believed to be absorbed in the photodoped layer close to the interface X–Y.

(Adapted from: P.J.S. Ewen and A.E. Owen, in, *High performance Glasses, Blackie and Son, 1992)*
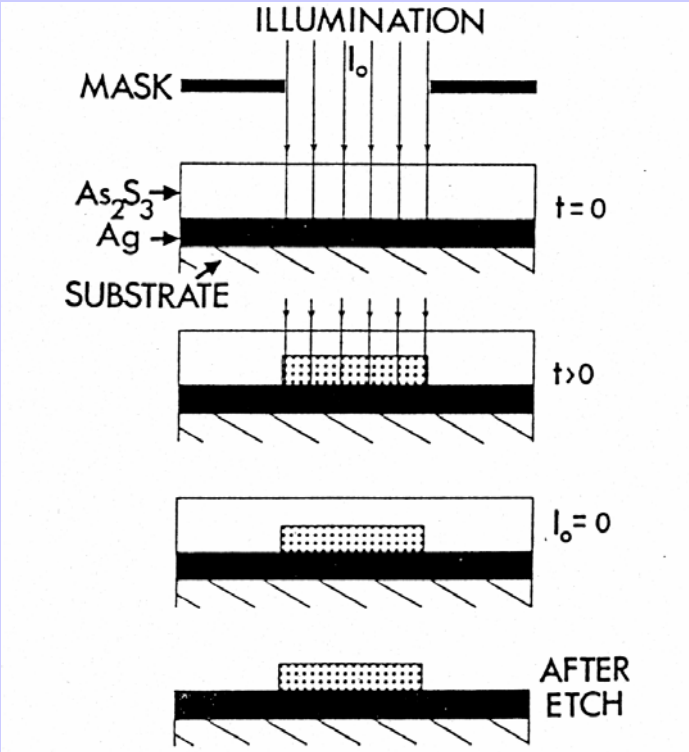
It has been found that the X-Y interface is usually rather sharp and that the metal concentration throughout the doped layer is approximately constant, or step-like. Photodissolution can be excited by photons with energies between ~ 250 – 800 nm, either by the ChG film side or, for very thin metal films, from the metal side, including, therefore, sub bandgap energy photons. Evidence for structural changes during photodissolution has been obtained by Raman and EXAFS spectroscopies.

Ag and S concentration profiles (relative to As) in Ag-doped a-As_2S_3 obtained by electron microprobe X-ray analysis (Matsuda and Kikuchi, 1973); (a) is for photodoped material and shows the 'step-like' Ag profile; (b) is for thermally doped material and shows a more gradual variation in Ag concentration in the interface region between the doped and undoped materials.

(Adapted from: P.J.S. Ewen and A.E. Owen, in, *High-performance glasses*, Blackie and Son, 1992)

The photodissolution effect is one of the most important, from the viewpoint of applications. This figure shows how images are formed

Schematic illustration of pattern formation by metal photodissolution using the Ag/As–S system. Ag dissolves into the chalcogenide in the illuminated region but not in the masked areas. Because there is negligible sideways migration of the Ag, a faithful image of the mask is produced in the chalcogenide and the photodoped region has an approximately rectangular cross-section. If illumination is terminated ($I_0 = 0$) there is no further movement of the Ag and an embedded structure is formed. A surface-relief structure can be produced by removing the undoped material with an alkali etchant.

(Adapted from: P.J.S. Ewen and A.E. Owen, in, *High performance glasses*, Blackie and Son, 1992)

Although, at room temperature, the metal ions diffuse into the glass only if under illumination, at higher temperatures (e.g. > 175 ^{o}C for the Ag-As$_2$S$_3$ system), thermally stimulated isotropic diffusion of the metal ions and degradation of the stored image may occur.

The technology of inorganic resists based on photoinduced effects in ChG (particularly the metal photodissolution effect) has been extensively studied, as a higher resolution alternative to the current technology, based on organic polymer photoresists. The main shortcoming of chalcogenide resists, at present, appears to be their sensitivity, which, for conventional optical illumination, is typically 3-5 times poorer than that of organic photoresists.