Ag doped chalcogenide glasses and their applications

Miloslav Frumar*, Tomas Wagner

University of Pardubice, Research Center LN00A028, Legions Sq. 565, 532 10 Pardubice, Czech Republic

Received 10 March 2003; accepted 5 June 2003

Abstract

Ag-doped chalcogenide glasses and amorphous thin films, their preparation, properties, photodoping, photoinduced surface deposition and applications, are reviewed, expanding on the results obtained recently. The progress obtained is not only connected with better understanding of their structure, chemical bonding and properties but also in application of Ag-containing glasses and films in solid-state batteries, electrochemical sensors and optoelectronics (gratings, microlenses, waveguides, optical memories, non-linear effects).

Keywords: Amorphous chalcogenides; Silver doping; Properties; Applications

1. Introduction

Ag-doped chalcogenide glasses and thin films have become attractive materials for fundamental research of their structure, properties, and preparation. They have many current and potential applications in optics, optoelectronics, chemistry, and biology (optical elements, gratings, memories, microlenses, waveguides, bio- and chemical-sensors, solid electrolytes, batteries, etc.). Some problems of their structure, properties, and applications have already been reviewed [1–**10]. Considerable interest has been paid to the problems of photodissolution and diffusion of Ag in bilayer structures of Ag/chalcogenide [1–*9]. In this paper, new data and results obtained recently are described and discussed.

2. Preparation

Glasses doped with silver (Ag) can be prepared by classical methods of synthesis for chalcogenide glasses (direct synthesis from elements or compounds in evacuated ampoules), or by doping of chalcogenide glasses by silver or silver compounds including AgX (X=Cl, Br, I), Ag₂Ch (Ch=S, Se, Te), or by other methods. In all cases, either homogeneous or phase-separated (composite) [**10–*13], or nano-particles containing glasses are obtained (see, e.g. Ref. [*14]). In many Ag containing glasses, two glass-forming regions were found, e.g. in glassy systems Ag–As–S, Ag–As–Se [**7,11,15], and Ag₂Se–Ga₂Se₃–GeSe₂ [16]. By heating of phase separated Ag₉(As₀₄Se₀₆)₉₁ glass to 120°C, the samples become homogeneous, as can be judged from impedance spectroscopy [11]. This fact is in accordance with the higher solubility of Ag in chalcogenides at higher temperatures. The glasses of the Ge–Se–AgI system with large Se content also appear phase separated; while glasses of this system with lower Se content based on Ge–Se face sharing tetrahedral units are homogeneous [*17].

Ag-doped glasses and thick films can also be prepared by the sol–gel method, or by silver ion exchange from solutions or melts [18]. Thick films can be prepared by the spin-coating technique, e.g. from n-butylamin solutions [19]. In such a case, the prepared films might contain excess solvent, which can be removed by vacuum heating of the film.

Thin amorphous films of Ag-containing glasses have mainly been prepared by thermal vacuum evaporation [20], sputtering [21], chemical or electrochemical deposition from solutions, by flash-evaporation [22,23], and also recently by the pulsed laser deposition method [24,25]. In addition, the Ag containing films can be prepared by so-called photodoping of chalcogenides, where a bilayer (Ag or Ag compound)/chalcogenide is illuminated by light or exposed by an e-beam. The silver is then dissolved in chalcogenide, forming systems Ag–As–S, Ag₂S–GeS–
such a method in the system Ag–As S [28,29]. Ag, the As–As correlations disappeared but the Ag–Ag interactions were demonstrated by or intermediate-range order. At higher concentrations of Ag, the As–As correlations disappeared but the Ag–Ag correlations’ peak increased in intensity, reflecting the direct contacts of AgS pyramids, similar to those seen in many silver-rich chalcogenide glasses [**10].

In Ag doped chalcogenide glasses and films ionic interactions between Ag⁺ and C₁ should be present because the Ag⁺ doped glasses are good ionic conductors. The Ag⁺ diffusion activation energy decreases with increasing Ag concentration [**34,35].

In 0.5[(1−x)Rb₂S−xAg₂S]−0.5GeS₄ glasses [38], x = 0.1−1, each mobile Ag⁺ cation forms its own specific environment that is not influenced by the presence of dissimilar cations. The non-linear dependences of properties on Ag content were found, e.g. for values of glass transition temperature, T_g, and for electrical conductivity, which probably results from cation-triggered rearrangements of the local polyhedra towards a more homogeneous glass structure [38].

The structure of Ag–As–Te glasses, studied by neutron diffraction, revealed nearly no changes of short and intermediate range orders when the content of Ag was low. At higher Ag content, the Ag coordination number becomes higher than 4, and, surprisingly, no significant ionic conduction was found in this system, which is attributed to compact As–Te network that restricts pathways, along which the Ag⁺ ion can move [39]. The X-ray analysis of (AgₓTe)₀.(AsTe₁−ₓ) glasses with x = 0 to 0.3, revealed that As atoms remain three coordinated, Ag atoms are roughly four-fold coordinated with Te atoms. The coordination of Te atoms increases from 1.93 to 3.60 with increasing Ag content [40].

A review on dynamics and structure of ionic transport in chalcogenide glasses is given in Refs. [**10,**41].
A $^{109}$Ag NMR study of highly conductive and macroscopically homogeneous glass $0.525\text{Ag}_2\text{S} + 0.475(0.5\text{B}_2\text{S}_3 + 0.5\text{SiS}_2)$ revealed three kinds of Ag$^{+}$ ions in sites with different chemical shifts in Ref. [42]. The silver ions move fast within separated clusters, but exchange among the three different clusters is relatively slow.

The structure of the films prepared by step-by-step reaction is similar to the structure of films and glasses of this system [43].

4. Physico-chemical properties

When compared with undoped glasses, the Ag-containing chalcogenide glasses and films exhibit a higher index of refraction, a red-shifted absorption edge, and decreased sensitivity for alkaline etching. Their optical transmittance, reflectivity and the coefficient of the optical non-linearity, $\chi^{(3)}$, is increased [43]. The values of glass transition temperature, $T_g$, decrease steeply for small concentrations of Ag ($x \leq 0.1$) and then increase slightly.

The optical gap $E_g^{\text{opt}}$ of Ag$_{x}$(As$_{0.33}$S$_{0.67})$$_{100-x}$ photo-doped films decreased with increasing content of Ag from 2.45 eV ($x = 0$) to 1.9 eV ($x = 0.41$), while the index of refraction increased from 2.38 to 2.8 [30]. The results are in agreement with other papers of this type. Even higher index of refraction (up to 3.3) was found in Ref. [45] for telluride glasses of the Ag–Se–Te system. They can contain up to 20 at% Ag (e.g. in Ag$_{20}$Se$_{70}$Te$_{10}$) forming homogeneous glasses.

The Ag–As–S glasses and Ag–As–Se films have similar properties [*46].

The Ag$^{+}$ doped glasses are ionic conductors [*10], for example in AgAsS$_3$ glass the conductivity is $\sigma = 10^{-5}$/Ω cm, and is governed by Ag$^{+}$ ions, while electronic (holes) conductivity is three orders of magnitude lower. Complete electrical conductivity spectra of 0.5Ag$_2$S–0.5GeS$_2$ glasses were studied and analyzed in broad temperature and frequency ranges in Ref. [47]. The addition of Ag to chalcogenide glasses (up to 57.1 at% for GeS glasses) increases the electrical conductivity by up to 22 orders of magnitude (for 30 at% of Ag). This increase is due to increased ionic conductivity of Ag$^{+}$ ions [32]. Generally, chalcogenide glasses, containing more than 5 at% Ag, are good ionic conductors [*10,32], the glasses with Ag content above 30 at% can be considered as superionic conductors [*1,47].

Bychkov found in Ag$_2$S–As$_2$S$_3$ glasses three regions of ionic conductivity and of silver transport numbers [*48]. The first one, with $x_{Ag} < 30$ ppm and small silver transport number; the second region, (30 ppm $< x_{Ag} < 1–3$ at%), which he calls critical percolation domain, and then the so-called modifier controlled domain. $x_{Ag} > 10–15$ at% Ag. In spite of the steep increase of silver ion transport numbers (and of electrical conductivity as well), the threshold, which was found below 1 at% Ag (Fig. 1) is hardly acceptable in usual models of percolation, as the critical concentration of the more conductive phase for percolation is generally, $p_c \approx 10\%$. This discrepancy is overcome by the so-called allowed volume approach (Fig. 2) [*48], which suggests that the Ag is free to move inside a relatively large volume of (1.6–2.5) nm$^3$ (percolation clusters), that are interconnected at lower content of Ag than in classical percolation.

Gotoh et al [*49] studied photoinduced anisotropy of ion conducting Ag–As–S.
The AgAsS$_2$ and AgGeS$_2$ glasses are stable in alkaline non-oxidizing solutions, but they can be dissolved in a 0.1 M NaOH + 0.9 M NaNO$_3$ solution at higher temperatures [50].

5. Photodoping

This effect was discovered more than 30 years ago and reviewed several times, e.g. in Refs. [1–*9,*51]. Photodoping, or photoinduced dissolution, is the effect when a film of Ag or Ag-compound is illuminated (UV, VIS, electrons) in contact with a chalcogenide layer or bulk glass, and the silver is dissolved in chalcogenide by a photochemical reaction. In such a way, many materials, e.g. As–S, As–Se, Sb$_2$S$_3$, Ge–S, Ge–Se, As–Te, Si–S, Se–Te, Ge–Se, Ge–S, Ge–Sb–S, (As$_{0.33}$Te$_{0.67}$)$_{100-x}$Te$_x$, and others can be doped [1–*9,11,19,45,*51–*57]. The sensitivity to radiation is relatively high, but it is lower than the sensitivity of silver halides in the photographic process. A number of models were proposed to explain this phenomenon [1–*5,12,30,55]. The composition of photodoped layers depends on conditions of their preparation (thickness and composition of chalcogenide, thickness of Ag, temperature, conditions of exposure, etc.).

The dissolved silver diffuses into the volume of chalcogenide and thus the photodoping gives relatively thin Ag-doped films. Deeper Ag-doped patterns can be prepared by illumination of multilayers of alternating Ag–chalcogenide–Ag–chalcogenide, etc. [26].

Photodoping in a chalcogenides has several typical features:

- The dissolution and diffusion of metals can proceed even in the dark, their rates are much lower without illumination. The concentration profile of photodoped metal not only obeys Fick’s law; it is often of step-like form with a sharp diffusion front (Fig.3) [**7,12,30,31].
- Large amounts of Ag can be dissolved in amorphous chalcogenide layers, in general up to 30–40 at% [30,*33,43,55] and in the case of GeS$_3$, up to 57 at% [32].
- The diffusion of Ag$^+$ follows the direction of light and very sharp edges between doped (exposed) and undoped (non-exposed) areas can be obtained. As a result, optical gratings, waveguides and high-resolution photoreists, can be prepared and produced.
- The optical transmittance of doped parts is decreased, and the absorption edge is shifted towards the long-wavelengths part of spectrum by doping.
- Diffusion is much quicker when the dielectric substrate is covered by a conductive film [**7] or when the chalcogenide is deposited on an electrically conductive substrate; the lateral diffusion (perpendicular to the direction of light) is much quicker [58,*59]. In this case, the electrical Coulomb potential, formed on the interface doped–undoped part of chalcogenide is apparently lowered by the conductivity of the substrate [**59] and the diffusion of metal ions can also proceed in the lateral direction.

- The rate of Ag dissolution depends strongly on the composition of chalcogenide [12]. The photoinduced dissolution and diffusion of Ag$^+$ proceeds more quickly in films with an excess of sulfur [60], which suggests that excess chalcogen plays an important role in the reaction with silver.

The mechanism of silver photodoping is not fully understood [1–**7]. The whole process of photoinduced dissolution and diffusion of metals in a-chalcogenides apparently consists of several steps. At the interface between silver and silver-doped chalcogenide it proceeds through the ionization of Ag

\[
\text{Ag} + \text{h}^+ = \text{Ag}^+ + \text{e}^-, \quad (1)
\]

in which silver atom captures prevailing free carrier from chalcogenide (hole) or loses its electron. As a result, very mobile Ag$^+$ ions are formed. Ag metal can also react with excess sulphur of the chalcogenide, e.g.:

\[
\text{Ag} + \text{S} = \text{Ag}^+ + \text{S}^-, \quad (2)
\]

or

\[
2\text{Ag} + \text{S} = 2\text{Ag}^+ + \text{S}^{2-}, \quad (3)
\]

or reduce the chalcogenide, e.g.

\[
\text{Ag} + 2\text{As}_2\text{S}_3 = \text{As}_4\text{S}_4 + 4\text{Ag}_2\text{S}. \quad (4)
\]

The Ag is oxidized to the Ag$^+$ ion (Eqs. 1–4).
reduction of As₂S₃ in Ag–As–S system goes to As₂S₅ but not to formation of free As–As bonds as determined from Raman spectra, because the Raman band near 234 cm⁻¹ corresponding to As–As vibrations does not change its amplitude during the photodoping. The products of reactions (1)–(4) remain dissolved in the amorphous matrix. The increased content of As₂S₅ structural units was found in thin film Raman spectra.

Similar effects as in Ag–As–(S, Se) systems were found in the system Ag–GeSe₂. Photodoped Ag⁺ ions form at first the phase close to Ag₂Se. The GeSe₂ and Ag₂Se have very close heats of formation: −10.8 and −9 kcal/mol and further Ge–Ge bonds are formed [**14,*64].

The schematic equations (1)–(4) describing dissolution of silver in amorphous chalcogenides are in fact parts of chemical reactions, which can be described for selenides, e.g. by:

\[
2\text{Ag} + \text{Se} = \text{Ag}_2\text{Se}; \Delta G^0_{298} = -25.13 \text{ kJ/mol}, \quad (5)
\]

\[
4\text{Ag} + 2\text{As}_2\text{S}_3 = 2\text{Ag}_2\text{Se} + \text{As}_2\text{Se}_4; \Delta G^0_{298} = -12.365 \text{ kJ/mol}, \quad (6)
\]

\[
6\text{Ag} + \text{As}_2\text{S}_3 = 3\text{Ag}_2\text{Se} + 2\text{As}; \Delta G^0_{298} = -8.155 \text{ kJ/mol}. \quad (7)
\]

During the photodoping process, all resulting compounds equations (5)–(7) do not usually crystallize and remain dissolved in an amorphous matrix. The \(\Delta G^0_{298}\) of reactions (5)–(7) is negative; these reactions can thus proceed spontaneously even without illumination as already mentioned. The values of \(\Delta G\) of reactions (5)–(7) are further decreased by the mixing entropy part \((-T \Delta S_m\) due to dissolution of the resulting compounds in glassy matrix. At higher Ag content, the Ag-rich phase can be separated as shown by electrical conductivity measurements [11].

The exposure of the interface of the metal/chalcogenide or of the interface of the doped–undoped part to light of energy close to the band gap of chalcogenide creates electron–hole pairs and the process of photodoping is quicker. When the interface of the doped/undoped part of the chalcogenide is exposed, the free holes, which prevail, and charge carriers in the undoped amorphous chalcogenides, diffuse together with mobile Ag⁺ ions into the undoped part of chalcogenide. The free electrons are captured more quickly. Due to this process, a Coulomb potential is formed on the interface of doped/undoped part of a-chalcogenide [12,*57–60]. This potential slows down, and eventually, stops further movement of the Ag⁺ doped front. When the chalcogenide is illuminated, newly created electrons and holes lower this Coulomb potential; Ag⁺ ions can then move (diffuse) further. Generally, the free electrons and holes are created mainly in the illuminated part. Due to the extremely small diffusion length of free carriers in highly disordered amorphous solid, their lateral diffusion (perpendicular to the direction of light) is extremely small. Very sharp concentration edges can be received between illuminated and unilluminated parts of a-chalcogenide [60].

In Ag–As–S and Ag–As–Se systems, the step-like form of the Ag⁺ diffusion profile can be also explained by diffusion in a two-phase system [12,58], because two glass forming regions divided by relatively large immiscibility region exist in Ag–As–S, Ag–As–Se systems and also in the Ag–Ge–S(Se) system. The step-like profile of the diffusion edge of Ag⁺ in chalcogenide films [58] was also confirmed by Rutherford back-scattering spectroscopy (Fig. 3, [31]). The possibility of reaching an Ag-content from 1 to 27 at% contradicts the model of a two phase-system diffusion [31,58]. The amorphous films are further from equilibrium than glasses and formation of a new phase (phase separation) could be very slow. So, many non-equilibrium states can be formed.

The kinetics of Ag dissolution fits a model with two stages with different diffusion rates [**7,61], with exponential dependence in early stages of diffusion, and linear dependence in further stages, \(f(t) = -a \exp(-bt) + ct + d\) (Fig. 4) [31,53]. The two-stage (exponential and linear) dependence of diffusion depths was found not only for vacuum evaporated films, but also for the thick films prepared by spin-coating [52]. It is surprising, that contrary to large changes of composition, the thermal constants of pure and doped films are changed only slightly (Fig. 5 [43,54]).

The solubility of Ag⁺ doped parts of chalcogenide films in alkaline solvents becomes very low as compared with...
precipitated Ag forms on the surface small clusters or crystals with a typical dimension of 10 nm in diameter and 1 nm in thickness \[68,69\]. The segregated Ag particles can be dissolved again in the amorphous chalcogenides after their annealing at higher temperatures and the process can be repeated many times \[*70\]. The optical transmission and reflectivity of the exposed (phase separated) and annealed (homogeneous) parts of sample are different. The sensitivity of photoinduced silver deposition is higher than the sensitivity of other photoinduced effects in amorphous chalcogenides; it is still lower than the sensitivity of silver halide photographic process. An excellent review on this subject was published recently \[**4\].

The explanation of photoinduced silver deposition can be based on thermodynamical consideration or on the hole–ion process. The hole–ion process explanation suggests that the optically created electrons are captured in illuminated parts, while more mobile holes move away from illuminated spot. The illuminated part becomes negatively charged and attracts the Ag ions, and, eventually, precipitates them as Ag neutral atoms \[68\]. Such a process can be a part of the decomposition of oversaturated Ag solid solutions. When the content of Ag is lower, only an increase of Ag density (chemical modification) in illuminated parts is obtained.

Using a thermodynamic approach, we can presume that the amorphous chalcogenides are oversaturated with Ag at lower temperatures. After illumination, the low temperature metastable system is approaching equilibrium and excess Ag is segregated on the surface. By annealing of the segregated system at higher temperatures, the excess Ag can be dissolved again due to increased solubility of Ag at higher temperatures. When the amorphous chalcogenide is cooled, the metastable oversaturated solution of Ag in amorphous chalcogenides is obtained again and the process can be repeated.

The optical reflectivity of a chalcogenide surface with silver islands is increased, when the silver is dissolved, the reflectivity of the surface decreases. This process has been proposed for the production of optical memories \[*6\]. The heating can be done by a laser beam where the contrast obtained can be very high. The addition of gold (Au), in a manner analogous to conventional photography, increases the photosensitivity of the photodeposition process \[67\] by at least two orders \[*6\]. The Au can form clusters, which behave as nucleation centers for Ag precipitation.

6. Surface silver photodeposition

The opposite process to photoinduced metal dissolution in a-chalcogenide is the photoinduced deposition of metal from metal-doped a-chalcogenide films or glasses on their surface \[1,**4,66,67\]. In this effect, the illumination induces diffusion of Ag\(^+\) ions to the surface and precipitation of Ag from Ag-rich Ag–As–S, Ag–Ge–S, Ag–Ge–Se and Ag–As–Se or other glasses \[**4\] with higher Ag content. In the \((\text{Ge}_{0.3}\text{S}_{0.7})_{100-x}\cdot\text{Ag}_x\) or \((\text{Ge}_{0.3}\text{Se}_{0.7})_{100-x}\cdot\text{Ag}_y\) glasses, the silver is precipitated on the surface, when \(x>45\), and, when \(y>22\) \[68\]. The

7. Applications

There are many current and potential applications of Ag-doped chalcogenide glasses and films such as solid electrolytes (batteries, thin film batteries), electrochemical sensors, photoreists, optical waveguides, diffraction elements, Fresnel lenses, optical memories, holography and other optical and non-linear optical elements \[1–**7\].
While the electrochemical sensors are based on the interaction of Ag⁺, built in the glass, or of amorphous thin film with Ag⁺ or other ions in the solution, the optical applications explore the potential of good transmissivity in IR spectral region, the high index of refraction and its increase with Ag doping. Their applications as photoresists and the production of etched gratings and waveguides and other optical elements, profit from the large decrease of etching rates of doped chalcogenides in alkaline solutions as compared with undoped films and bulk samples [50]. As the Ag content in a-chalcogenide can also be increased by photodoping, very complex patterns can be formed by exposition of Ag/chalcogenide bilayers by light or electron beam.

The Ag doped glasses can be used as optical memory materials (see sections: surface silver deposition, phase-change optical memories) and materials for holography. The sensitivity can be increased by the simultaneous application of an electrical field with light [6]. Very promising results were obtained with Ge–Se–AgI and Se–Ag–I glasses [6]. Photodissolved silver in a-chalcogenides can be used in relief images in optical elements, in microlithographic schemes and for direct imaging by photoinduced silver deposition. Many chalcogenides, and especially the Ag-doped chalcogenides, possess a high non-linear coefficient χ (4) [44] and can potentially be applied in optical signal processing. Nanometer dimension lines (patterns) can be formed by a focused laser beam [71]. The width and height of Ag-doped lines can be influenced by beam parameters, such as accelerating voltage [71].

The Ag-doped binary and ternary tellurides, e.g. Ag₅Ge₁ₓTe₄₋ₓ (2.5 ≤ x ≤ 21.5) are becoming important because some of them are used as materials for phase-change optical storage (DVD disks, etc. [72]). They exhibit single glass transition and single crystallization temperatures, which is important for rewritable disks [72].

For fabrication of waveguides, laser-beam writing, wet etching methods and local metal doping can be applied [73]. The attainable change of index of refraction is high (Δn = ∼0.4, or more), this allows formation of well-confined structures. The waveguides can be prepared by thermally activated silver diffusion in chalcogenide films [73], when silver is evaporated on the substrate, the desired patterns are formed from silver using photoresists, and etching in nitric or phosphoric acids removes the excess Ag. Then the chalcogenide film is evaporated on the substrate with silver patterns. Subsequent heating causes silver dissolution and formation of waveguides with an increased index of refraction in the doped parts [73]. Post-deposition annealing of the films (∼145°C, 2 h) was necessary for stabilizing of As₅S₃ films. Without annealing, the thickness and index of refraction was steeply changed [73]. We believe, that such changes result from micro-inhomogeneities in the fresh-evaporated As–S films [74].

Ag doped chalcogenides with higher Ag content are ionic or superionic electrical conductors (Fig. 1 [78]). Three transport regimes were found in these glasses [78]: (a) below the percolation threshold — the glasses are ionic insulators; (b) above percolation threshold — the glass can be described by a modified percolation model. In this region, the conductivity depends on host matrix, or more precisely, on the dimensionality of the vitreous matrix as would be expected; (c) far above the percolation threshold, the ion transport depends on the Ag content but not on the host matrix, see above.

The glassy chalcogenides with mixed cations, e.g. 0.5(1−x)Rb₂S−xAg₂S−0.5GeS₂, x = 0.1–1 are also applicable as solid electrolytes [38].

The Ag-doped chalcogenide glasses and thin films, e.g. of the composition of AgAs₅S₂ and AgGeS₂ can be used as sensitive electrochemical electrodes or their membranes for sensors for potentiometric determination of Ag⁺, Se²⁻, S²⁻, Pb²⁺, Cd²⁺, and other ions [75–77]. They have high ionic conductivity and are resistant to acidic solutions [50]. These glasses are also resistant to the action of alkaline non-oxidizing solutions (the dissolution rate is only ~6 × 10⁻⁶ g/cm² h in 10⁻² M NaOH). The activation energy of such dissolution was (70–99) kJ/mol [50]. Multicomponent films for electrochemical sensors are difficult to prepare, because of the dissociation and fractional evaporation of individual components of the glass. A possible solution is pulsed laser deposition (PLD) where the bulk material is ablated by high-energy excimer laser pulses and deposited on a substrate. In such a way, samples with complex composition, such as CdS–AgI–As–S, Ti–Ag–As–I–S, Pb–Ag–As–I–S were prepared [76,77]. The stoichiometry of the target material is mostly maintained when the PLD is used. Prepared films, when used as electrochemical sensors, possess high sensitivity for several ions.

Various compositions of Ag⁺ chalcogenide were proposed as solid electrolytes for batteries [38,75].

As mentioned earlier, Kawaguchi and coworkers [66–68,70] studied intensively the so-called ‘photoinduced surface deposition’ and its possible applications for optical recording.

A new type of electrical memory was proposed in Ref. [78]. The electrodes are prepared in contact with an Ag photodiffused layer, with an anode of oxidizable Ag and the cathode of an inert conductor. When a voltage is applied, the Ag⁺ ions are reduced on the cathode and this deposition could extend from cathode to anode and short-cut the circuit. The electrical resistance drops by many orders of magnitude because of metallic conductivity. A reverse bias could cause the dissolution of Ag link, and the original state is obtained. The write–erase cycle may be repeated tens of million of times [78]. The reading voltage would be lower than the writing–erasing one.

Rewritable recording materials of a Ag–In–Sb–Te system, namely Ag₈In₁₄Sb₅₅Te₂₃ were studied in Ref.
The erasing mechanism in rewritable CD disks based on Ag–In–Sb–Te depends on erase power and linear velocity of the media [81]. Under lower velocity and low laser power, the nucleation and growth mechanism is most important. At higher laser power, the grain growth controls the mechanism of erasing. When the linear velocity is further increased, the erasing originates from the interface between amorphous marks and their neighbouring crystalline region [80]. While in Ge–Sb–Te films, nucleation driven mechanisms is controlling the rate of crystallization, in Ag–In–Sb–Te films the controlling process is growth-driven crystallization [80]. The rate of crystallization is also influenced by the thickness of recording layer and by interface layers as well [80]. The active layer can be transformed into different phases after applying different initialization powers. For lower power, rhombohedral Sb crystals were formed, for higher power AgSbTe2 and Sb crystals were formed in the Ag–In–Sb–Te film [82].

The optical properties of phase-change memory films depend on the conditions of magnetron sputtering and proper gas pressure and scattering power are important for phase-change films with good properties.

**Nanometer dimension lines** (patterns) for different applications can be formed by focused laser beam in Ag doped chalcogenides [71]. The width and height of Ag-doped lines can be influenced by beam parameters such as accelerating voltage [71].

Diffraction gratings can be prepared from Ag photo-doped chalcogenide films, such as As2Se3–Ag, As2S3–Ag, e.g. Refs. [84,85]. When the amorphous As20Se80 was coated with two metal layers (Au, Ag) [86], the sensitivity was dependent on the sequence of the coatings. Very good diffraction efficiencies were also obtained for glasses from the Ag–Se–I system, particularly for Ag13Se7I12 [6].

Silver nanoparticles (silver dots), which can be formed in chalcogenides, can be used for ultrafast optical switching (fs).

### 8. Conclusion

The family of Ag-doped chalcogenides includes interesting materials with many applications and understanding of their properties is rapidly progressing. In spite of that, many problems still remain, partly because the amorphous state is a strongly non-equilibrium one and its ‘distance’ from equilibrium can be very different. This fact gives many opportunities to control properties over broad ranges but makes it sometimes difficult to interpret these properties. Although many papers are cited in this review, the selections are not comprehensive. The description and interpretation in mainly based on present authors’ point of view, which is not necessarily the common understanding of the glass community.

### Acknowledgements

The work was supported by Ministry of Education of Czech Republic under the project LN00A028. Their support is highly acknowledged.

### References

Papers of particular interest, published within the annual period of review, have been highlighted as:

* of special interest;
** of outstanding interest.


Akai T, Martin SW, Borsa F. Chemical and dynamical speciation of mobile ions in the glassy fast ionic conductor Ag,S+3 Ba,S+3 +S6;2−. A 57Ag nuclear magnetic resonance study. Phys Rev B: Condens Matter Mater Phys 2001, 63(2): 024303-1-024303/7


