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Ageing of $Ge_{24.9}Sb_{11.6}S_{63.5}$ thin films under various conditions

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HIGHLIGHTS

- $Ge_{24.9}Sb_{11.6}S_{63.5}$ thin films were aged under various conditions.
- Ageing leads to the self-bleaching or bleaching depending on the storage conditions.
- Photo-sensitivity of thin films was decreasing during the ageing.
- The overall kinetics of ageing was well described by stretch-exponential function.
- The films were monitored by spectroscopies, AFM, ellipsometry and tenziometry.

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ABSTRACT

Amorphous $Ge_{24.9}Sb_{11.6}S_{63.5}$ thin films prepared by thermal evaporation were aged for more than 1 year under various conditions: in the dark in a desiccator, in a dark and humid atmosphere and under laboratory conditions under daylight. The bleaching of thin films (the blue shift of the optical band gap) was observed with the magnitude depending on the storage conditions. The overall kinetics of ageing (bleaching) follows well the stretch exponential function with the formal rate depending on the storage conditions and the stretch exponent slightly varying in the region of 0.54–0.6. The photo-sensitivity of the aged thin films was significantly affected by storage conditions and was found to decrease with the increasing time of ageing. The changes in thin films during the ageing were monitored with respect to the chemical composition, the structure, the surface wettability, the surface topology and information about the depth and optical parameters of the formed over-layer and were finally correlated with the storage conditions.

1. Introduction

Chalcogenide glasses and amorphous thin films are the subject of numerous studies particularly due to their unique properties such as a broad optical window, a high refractive index, a low phonon energy, photosensitivity and phase-change [1]. Such properties make these materials attractive for a wide range of applications such as in sensors and detectors, lasers, optical fibers, waveguides and phase-change memories. Although the chalcogenide glasses and amorphous thin films find application in a number of fields, the limitation of such materials could be the

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uncontrolled drift in their exploitation characteristics over time [2,3]. This phenomenon is known as ageing and restricts the wider practical implementation of these materials. The ageing of the virgin/as prepared material originates from the thermodynamically non-equilibrium state of the glasses and amorphous thin films. This means that the properties can vary over a period of time as the state tries to reach a more energetically favorable state. Moreover the ageing process can significantly by modified by external conditions of ageing namely by an interaction with the environment and even a day light. Despite extensive research on ageing, the current understanding of the exact nature of this phenomenon is still incomplete. The structure stabilization of the amorphous thin films and glasses can be achieved by annealing at a temperature below the glass transition temperature [4,5]. During temperature annealing, removal of the metastable states, "wrong" homopolar bonds, stress and other defects connected with the virgin/as prepared material occur. Hydrolysis/oxidation can still proceed, however, even on the surface of the annealed thin films [5]. For the purpose of this communication we shall use the term physical ageing only for the ageing which is the function of time and the temperature of the process. No other external influences are considered. In real conditions, however, the material in the course of ageing could be exposed to the ambient atmosphere and daylight and such ageing is further called daylight modified or hydrolysis modified ageing.

Over recent years, both the physical ageing and ageing of the bulk samples of some glasses, namely of the Ge-Se and As-Se systems, were studied in several papers e.g. by Golovchak and others [6–10]. Some, not exhaustive, conclusions can be summarized as it follows: (i) in Ge-Se system for under-constrained network both the short-term and long-term physical ageing was observed, while for over-constrained networks the long-term physical ageing was not observed. The process of ageing proceeds namely due to a phase separation process and to be well observable the higher temperatures of storage are necessary [8] and (ii) namely for Se-rich As-Se glasses the careful analyses of ageing kinetics indicates that physical ageing can be understood as superposition and/or sequent alignment-shrinkage processes having different relaxation times [10].

Light-assisted ageing of various mostly glasses of the Ge-Se and As-Se systems, were also studied in series of papers, see e.g. Refs. [11–16]. It was found that: (i) the connectivity of the backbone determines the magnitude of light-assisted ageing and it vanishes above the coordination number 2.4, (ii) above-band-gap excitation assists to elastic strains in the surface layer (the problem of the penetration depth of the above-band-gap light excitation), (iii) the band-gap light assists to the ageing by short-range order changes due to the bond breaking mechanism and possible formation of valence alternation pairs and (iv) sub-band-gap light excitation could contribute to ageing by inelastic photon scattering, by phonon-assisted transitions and by two-photon absorption see e.g. Ref. [15]. In this case we suppose, however, quite high photon flux should be used.

Over recent years, changes in chalcogenide films were studied due to improvement in the resolution and precision of the measurements tools. Charpentier et al. [17], for example, studied the "natural" (physical) and "protected" (modified) ageing of $Ge_{15}Sb_{20}S_{65}$ chalcogenide amorphous thin film for six months. The observed blue shift of the optical band gap value ($\approx$ 170 meV) was attributed to the diffusion of oxygen into the film and to the subsequent formation of Ge oxysulfides. In our previous work, the physical ageing phenomenon of the Ge-Sb-S thin film stored in a dark and dry atmosphere for 2 years was described as self-bleaching due to the blue shift of the optical band gap value by approximately 100 meV [18]. Additionally, the photo-sensitivity of the thin film decreased during the physical ageing. It was concluded that the physical ageing of Ge-Sb-S thin film was a consequence of network ordering as detected by FTIR spectroscopy and the formation of a thin over-layer of partially oxidized/hydrolyzed film as identified by EDX analysis.

The process of the relaxation of the illuminated chalcogenide glasses and amorphous thin films in a dark place was studied for binary and ternary systems [19–22] and the loss of the photo-induced record over time was monitored and correlated with the chemical composition and rigidity of the system.

In the present paper we study the ageing of variously stored $Ge_{24.9}Sb_{11.6}S_{63.5}$ amorphous thin film for more than 1 year without previous thermal stabilization. The above-mentioned chemical composition was used because the average coordination number is 2.58, assuming that the coordination numbers for Ge, Sb and S are 4, 3 and 2, respectively. We therefore expect the network of this film to be over-constrained following the Phillips–Thorpe [23] approach and that the ageing due to network relaxation will proceed quite slowly. In addition, the $Ge_{24.9}Sb_{11.6}S_{63.5}$ film is stoichiometric hence we expect the homopolar bonds (Ge-Ge, Sb-Sb, S-S) to only be present as wrong bonds and not as bonds forming the overall glassy network and that the ageing will not be significantly influenced by the presence of the weaker regular homo bonds as it could be in the case of under-stoichiometric films and glasses. Finally, the chemical composition of bulk $Ge_{24.9}Sb_{11.6}S_{63.5}$, i.e. $((GeS_2)_{0.8}(Sb_2S_3)_{0.2})$ ranks, in our experience, with fairly stable glasses and can be used for the preparation of thin amorphous films by simple thermal evaporation with a reasonably conserved chemical composition. Amorphous thin films were stored under different conditions: (i) in a dark and dry atmosphere, which is the storage form of thin films preventing the hydrolysis of surface and photo-induced effects (samples labeled as DES), (ii) in a dark and dry atmosphere with stable humidity enabling mainly hydrolysis/oxidation of thin films surface (samples labeled as RH75) and (iii) the last group of thin film samples was exposed to the daylight under laboratory conditions in order to simulate the role of daylight on the samples ageing (samples labeled as SUN). We examined: (i) the role of storage conditions on the magnitude of thin films bleaching as a consequence of ageing, (ii) the possible origin of observed bleaching and (iii) photo-sensitivity of thin films during ageing.

2. The experimental part

Amorphous films with a thickness of around 1100 nm were prepared by means of the vacuum thermal evaporation TE (Balzers BAE 250T coating system), p $\approx$ 10^{-3} Pa, rate of evaporation 2–2.5 nm s^{-1}) from previously synthesized stoichiometric bulk glass $(GeS_2)_{0.8}(Sb_2S_3)_{0.2}$ i.e. $Ge_{23.5}Sb_{11.8}S_{64.7}$ in atomic fraction) onto microscope glass and Si substrates. The chemical composition of the thin films was checked by an electron microprobe X-ray analysis (Jeol JSM5500 LV) and was found to be $Ge_{24.9}Sb_{11.6}S_{63.5}$ for all the prepared virgin thin films with a precision better than ± 1.5 at.%.

The ageing was studied for three groups of differently stored $Ge_{24.9}Sb_{11.6}S_{63.5}$ thin films: (i) in a dark and dry atmosphere in a desiccator labeled as DES (physical ageing), (ii) in a dark and humid atmosphere with a relative humidity equal to 75% obtained by a saturated water solution of NaCl [24] designated as RH75 (hydrolysis modified ageing) and (iii) stored at daylight behind a glass window at room temperature (25 °C) and humidity ($\approx$ 35%), SUN series (daylight modified ageing). The samples were exposed to the direct daylight, while they were partly shielded by the window-glass (which cut-off the light below 330 nm). The intensity of the daylight was monitored by the automatized hydro-meteorological