In Situ Measurements of X-Ray-Induced Silver Diffusion into a Ge$_{30}$Se$_{70}$ Thin Film

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High-resolution X-ray photoelectron spectroscopy is used to identify the mechanism of X-ray-induced Ag diffusion into Ge$_{30}$Se$_{70}$ chalcogenide glass thin films, which are prepared in situ to avoid oxygen contamination. From the analysis of Ge 3d, Se 3d, and Ag 3d core levels, and valence band spectra, changes in the electronic structure are determined as Ag diffuses gradually with increasing irradiation. The ternary phase based on Ge$_2$Se$_6$ units, which contains homopolar Ge–Ge bonds, forms when diffusion approaches equilibrium where Ag content ~30 at.%. The formation of a Se-rich precipitate, being detected in the near-surface region at the initial stage of the process, but the previously assumed Ag$_2$Se phase is not detected.

1. Introduction

Silver photodiffusion into chalcogenide glass (ChG) thin films has a variety of applications in microlithography for fabricating micro-electro-mechanical systems,\(^1\) very large-scale integrated circuits,\(^2\) programmable metallization cell structures for nonvolatile memory,\(^3\) etc. Thin films of the Ge-Se system are strong candidates for such applications because of their wide glass-forming region, relatively high glass transition temperature \(T_g\), and high doping ability. To optimize the processing parameters and composition of amorphous Ge–Se films, it is necessary to understand the evolution of silver diffusion and the final structure of the Ag-doped product during exposure to light.

Different experimental methods including Raman spectroscopy,\(^4\) Rutherford spectroscopy,\(^5\) electrical resistance measurements,\(^6\) secondary ion mass spectroscopy,\(^7\) modulated temperature scanning calorimetry,\(^8\) Moessbauer spectroscopy,\(^9\) X-ray diffraction,\(^10\) electron diffraction,\(^11\) optical spectroscopy,\(^12\) ellipsometry,\(^13\) grazing-incidence X-ray scattering,\(^14\) differential anomalous scattering,\(^15\) extended X-ray absorption fine structure (EXAFS),\(^16\) transmission electron microscopy,\(^17\) microlithography technique\(^18\), atomic force microscopy, and electron energy-loss spectroscopy\(^19\) have been used to obtain structural information connected with photodoping. In spite of this remarkable list of available data, the mechanism of electronic and structural transformations accompanying the photodiffusion of Ag into the Ge$_{1-x}$Se$_x$ matrix remains unclear. The amorphous character of the host limits the usefulness of these methods and the reliability of the data. Among the existing models, the one considering photodoping as a solid-state reaction triggered by light absorption or photoionization of hot Ag electrons appears to be the most promising.\(^17\) At the same time, the atomistic mechanism of photodoping, which strongly depends on the composition of the host film, is still controversial even for stoichiometric GeSe$_2$. Ag-induced phase separation, accompanied by the formation of Ag$_2$Se and a composition-dependent ternary phase, is the most well-known approach. Even then, the final “destination” of free electrons resulting from Ag photoionization remains unknown.

Therefore, in this work, we characterize the evolution of X-ray photon-induced silver diffusion by measuring in situ the chemical structure and composition of the near-surface layer of a Ge$_{30}$Se$_{70}$ chalcogenide glass film at various stages of photodiffusion by high-resolution X-ray photoelectron spectroscopy (XPS). This method provides information about electron redistribution due to structural transformations caused by the interaction of Ag with a ChG matrix. These measurements also offer the possibility of in situ monitoring of the effects of photodoping such that X-rays simultaneously serve as a probe beam and at the same time also as a source of irradiation that causes silver diffusion into the ChG film. To our knowledge, this work is the first attempt to investigate silver diffusion in germanium selenides by in situ high-resolution XPS. Previous low-resolution XPS studies could only indicate a qualitative trend of the changes in electronic structure due to silver diffusion into thin Ge-Se films.\(^18\)–\(^20\) By comparison, the present analysis of core-level spectra provides quantitative data on electron redistribution in the matrix, and hence a clearer picture of photodiffusion in these ChG films.

Our entire experiment, from the very beginning (thin film deposition) to the very end of the XPS measurements, has been conducted under ultra-high vacuum. Thus, we have observed “pure” photodoping effects without any influence of contamination from oxygen, which can significantly alter the process of silver diffusion as suggested earlier.\(^21\)

II. Experimental Procedure

A Ge$_{30}$Se$_{70}$ thin film (thickness $>$ 120 Å) was thermally deposited on an HF-etched Si substrate inside an XPS chamber under a vacuum of $\sim 10^{-7}$ torr in darkness, using bulk glass as the starting material. On top of the Ge$_{30}$Se$_{70}$ film, a silver film ($\sim$ 100 Å) was thermally deposited in a vacuum of $\sim 10^{-8}$ torr. There was no exposure to any oxygen-containing environment between the depositions.

High-resolution XPS spectra were obtained using a Scienta ESCA-300 spectrometer (AG Scienta AB, Uppsala, Sweden) with a monochromatic Al K$_\alpha$ X-ray (1486.6 eV) spot that was $\sim 3$–4-mm long and $\sim 250$-μm wide. Data acquisition was restricted electronically to a smaller region within the X-ray-illuminated area. The angle (θ) between the surface and the detector was 90°; for this condition, the maximum depth of analysis was $\sim 100$ Å. The spectrometer was operated in a mode that yielded a Fermi-level width of 0.4 eV for Ag metal. The residual pressure inside the analysis chamber was lower than...
The XPS data consisted of survey scans over the entire binding energy (BE) range and selected scans over the valence band, Auger peaks, or core-level photoelectron peaks of interest (Ge 3d, Se 3d, and Ag 3d$_{3/2}$). An energy increment of 1.0 eV was used for recording the survey spectra and 0.05 eV for the case of core-level spectra and Auger peak. The core-level and Auger peaks were recorded by sweeping the retarding field and using a constant pass energy of 150 eV. The reproducibility of the measurement was checked on different regions of a film. The surface charging from photoelectron emission was neutralized using a low-energy (<10 eV) electron flood gun, which minimized any distortion and shift of spectra. The gold 4f$_{7/2}$ core-level position at 84.0 eV was used as a reference. To analyze the evolution of spectra with time of irradiation, 10 sets of measurements were made under the same vacuum conditions. The duration for one complete set of measurements was ~40 min.

Data analyses were conducted with casaXPS software package. For analyzing the core-level spectra, a Shirley background was subtracted and a Voigt line shape was assumed for the peaks. The concentrations of appropriate chemical elements were determined from the area of core-level peaks taking into account appropriate sensitivity coefficients.

Each Ge 3d and Se 3d core-level spectrum was fitted to obtain sets of doublets representing the spin orbit splitting of d and p electron levels. The number of doublets within a given peak was determined by the goodness of fit. Only doublets that significantly improved the goodness of fit were considered. Splitting parameters (intensity ratio and peak separation) for the doublets of a particular element were chosen from the measurements of spectra of pure Ge and Se elements and their stoichiometric compounds in the same spectrometer. The full-width at half-maximum (FWHM) was assumed to be the same for the peaks within one doublet. However, different FWHM values were allowed for independent doublets of the same core-level peak. The same mix of the Gaussian (90%) and Lorentzian (10%) parts of the Voigt function was chosen for all doublets of a given core level. Our fitting procedure gave asymmetry values close to zero for all peaks. With these constraints, the uncertainty in peak position and area of each component was ±0.05 eV and ±2%, respectively. The exact positions of the component peaks depend on the corresponding environment of the atom, the oxidation number of the atom within this environment, the electronegativity of the neighboring atoms, and the type of chemical bonding. The core-level spectra were recorded at the same place several times one after the other.

III. Results and Discussion

The study of the silver photodiffusion process in a Ge$_{30}$Se$_{70}$ film by a high-resolution XPS method requires comparison of the shape and structure of Ge 3d and Se 3d core-level spectra for the as-prepared (i.e. undoped) and Ag-photodoped samples, as well as an analysis of the Ag 3d$_{3/2}$ core-level spectrum. Modified Auger parameter \( z = (X + C)/A \) (where \( X \) is the energy of the X-rays, \( C \) is BE of the appropriate core level, and \( A \) is the kinetic energy of Auger electrons) was used to determine significant structural changes (phase transformations, phase separations, and so on) around the given element.

The results of compositional analysis of the surface region showed a gradual decrease in the concentration of silver, clearly indicating radiation-induced diffusion. Ultimately, the concentration reached a plateau when the diffusion stopped. Even though the thickness of the Ag layer was close to the analysis depth (~100 Å), we were able to examine core-level spectra for all three elements because of active diffusion of silver inside of the sample and lack of evidence for metallic silver on the top of the sample during the first set of the measurements.

It is important to note that X-ray irradiation of the pure Ge$_{30}$Se$_{70}$ thin films inside the XPS chamber for 400 min did not produce any detectable changes in the XPS spectra of the sample. Thus, all the changes in XPS spectra discussed below are related to X-ray-induced silver diffusion only.

First, we would like to discuss the initial Ge$_{30}$Se$_{70}$ material. The Ge 3d core-level peak is situated at ~30.8 eV. It roughly coincides with the earlier data obtained by low-resolution XPS for GeSe$_2$ (~31.1 eV). The difference (~ ~0.3 eV) is explained by the lower precision of the measurement and referencing procedures in the latter case and does not relate to the variation of chemical composition. The fitting of the Ge 3d core-level peak for the nondoped sample (Fig. 1) reveals two pairs of peaks corresponding to two different environments of Ge atoms, despite the fact that we are dealing with a Se-enriched composition Ge$_{30}$Se$_{70}$ (in comparison with stoichiometric Ge$_3$Se$_2$). The major pair, positioned on the high-energy side (the parameters of the peak components are presented in Table I), as expected, is associated with Ge within Ge-Se tetrahedra (regular structural fragments, containing only Ge–Se bonds), which are the main structural blocks of Ge$_{30}$Se$_{70}$ thin films as well as bulk stoichiometric GeSe$_2$ glass.

The existence of a minor pair at lower energies suggests that in thin films of Ge$_{30}$Se$_{70}$ composition, “wrong” Ge–Ge bonds (and, respectively, additional Se–Se bonds) are formed besides dominant Ge–Se bonds. Such homopolar bonds in vacuum-evaporated Ge$_{30}$Se$_{70}$ thin films were detected earlier by the Raman spectroscopy method.

The concentration of the “wrong” homopolar bonds strongly depends on the conditions of thermal deposition. The analysis of spectra suggests that nearly 89% of all Ge atoms are within GeSe$_4$ and ~11% of them are within the units containing Ge–Ge bonds (the precision of such an estimation depends on the absolute concentration and the accuracy of the sensitivity factors, which does not exceed 3–5 at.%). Statistically, Ge covalently linked with one Ge and three Se is the most likely possibility for the formation of Ge–Ge homopolar bonds. In this case, we consider the option when Ge–Ge bonds are a part of ethane-like units Ge$_2$(Se$_1$)$_2$h (or some modification of these units) revealed previously in GeSe$_{25}$.

The Se 3d core-level peak in Ge$_{30}$Se$_{70}$ is positioned at ~54.3 eV, while Ueno observed it for GeSe$_2$ at ~54.7 eV. The possible reason for the ~0.4 eV difference is already explained above. Examination of the fitted Se 3d core level spectrum for the Ge$_{30}$Se$_{70}$ thin film (Fig. 2) confirms the existence of a Se–Se-containing minor component (~17% of all Se atoms), most probably associated with Se in the Ge-Se–Se–Ge fragments, which is situated at a BE (see Table I) higher than the major pair (~83% of all Se atoms) corresponding to Se atoms within regular Ge-Se-Ge units. The concentration of Se-Se in the as-deposited film is two times larger than the statistically calculated value for Ge$_{30}$Se$_{70}$ glass, indicating an over-existence of the “wrong” homopolar bonds after thermal deposition.
Fitting of any single core-level peak is less precise in comparison with fitting of a complex spectrum containing overlapped components associated with spin-orbit splitting (as in the case of Ge 3d and Se 3d). However, an analysis of Ag3d5/2 core-level spectrum just after the deposition of an ultra-thin Ag layer (≈ 100 Å) (Table I) clearly shows the existence of three different chemical states of silver (Fig. 3). To verify the origin of the components, we compare the results for the same core level after 10 consecutive measurements of the whole set of spectra (Ge 3d, Se 3d, Ag 3d5/2, Auger peaks for all three elements, and valence band spectrum) until an equilibrium state is established and no more changes in structure and hence diffusion in sample are detected. There are strong reasons to believe that already at the beginning of X-ray irradiation (i.e., the first XPS measurement), the silver layer on top of the ChG film is neither metallic (as in bulk Ag metal, usually situated at the 368.3 eV position,26 Fig. 4) nor fully ionized (such as in AgCl). First, the position of the Ag 3d5/2 peak for non bonded Ag ions is expected at a much higher binding energy (BE = 369.8 eV)27 than our highest component Ag(II) at 368.3 eV (Fig. 3, Table I). Second, this component does not disappear completely even at the equilibrium state after 10 measurements, thus excluding its origin in metallic silver. The FWHM of this component (0.81 eV at the beginning of X-ray irradiation) is also too large for metal–metal interactions as in a pure Ag layer. Therefore, a probable

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Table I. Fitting Parameters of High-Resolution XPS Core Level Spectra

Fig. 2. Fitting of X-ray photoelectron spectroscopy (XPS) Se 3d core-level spectrum for a thermally evaporated Ge30Se70 thin film.

Fig. 3. Fitting of X-ray photoelectron spectroscopy (XPS) Ag 3d5/2 core-level spectrum obtained just after deposition of a 10-nm Ag film onto a thermally evaporated Ge30Se70 thin film.
The chemical state of Ag associated with 368.3 eV (18 at. % of all Ag atoms) is metastable partly ionized Ag^{+} ion at the near-surface region; compared with an isolated Ag^{+} ion, its charge distribution is influenced by the electronic density of the ChG matrix. The existence of such silver species in a Se-rich metastable composition based on Ag^{+}–Se interactions very close to the surface is supported by the significant variation of the Se/Ge ratio with the irradiation time (2.8 and 2.5 at the beginning of irradiation and in the equilibrium state, respectively). This agrees with the earlier conclusions that Ag in ChG exists as Ag^{+} ions incorporated into the glass matrix.20 The significant decrease in the FWHM of the 368.3 eV component from 0.81 to 0.61 eV after prolonged irradiation may be an evidence of the stabilization of the Ag^{+}–Se interactions as silver diffuses into the ChG film. Both Ag 3d_{5/2} components at lower BE can be linked only with some Ag-containing phases. Their stability is confirmed by the low FWHM values. More detailed structural information can be proposed only after analyzing the influence of silver on the structure of Ge 3d and Se 3d core-level spectra.

The time-dependent effect of Ag diffusion into the film is clearly seen when comparing the valence band spectra of the samples just after Ag deposition and in an equilibrium state (Fig. 5). For clarity, intermediate spectra are omitted from the figure. The structure of Ag 4d peak at ~5.5 eV is much more complex at the beginning of Ag diffusion, revealing a distinct additional component at the low-BE side. Narrowing of the peak in the equilibrium state is evidence supporting stable ternary phase formation, when the diffusion process is accomplished.

Ag diffusion causes an ~0.5 eV shift (0.4 eV was reported by other authors) of the Ge 3d core-level peak to a lower energy (Fig. 6). This considerable change is a consequence of structural rearrangement with the complete disappearance of GeSe_{4} tetrahedral units, which are supposed to be the main structural fragments of a Se-rich Ge_{30}Se_{70} thin film.24 Instead of GeSe_{4}, the ternary composition, which contains Ge–Ge bonds, most probably within Ge_{2}Se_{6}-type structure, is proposed to be formed after Ag diffusion. The fit of the Ge 3d core-level spectrum revealed two pairs of peaks, confirming two distinct chemical states of Ge atoms in the matrix. We suggest that one of them, at a higher BE, is “pure” Ge_{2}Se_{6} and most probably the other is a Ge_{3}/C_{0} coordination defect, typical for chalcogenide glasses,29 within poorly developed ethane-like units. This assignment is based on the estimated chemical shift, caused by a change in the chemical environment and/or oxidation number of Ge atoms, with respect to the position of Ge within the GeSe_{4} tetrahedra. A considerable increase in the concentration of Ge–Ge bonds in the matrix after silver diffusion was observed earlier by Raman spectroscopy in Ge_{30}Se_{70} and even more so in Se-rich Ge_{20}Se_{80} thin films after Ag diffusion.4,30 However, the relatively large FWHM (~1.0 eV) value for both Ge 3d components still requires an explanation. It could be because of the different charge states of Ge atoms linked with Ge, thus introducing a distortion in electronic density around Ge atoms; we suppose that Ge_{2}Se_{6} units are not face shared as in the case of Ge-rich glass.31 Most of the Se atoms probably exist in the form of Se–Ag complexes,17 but some of them could form regular covalent Ge–Se–Ag fragments.

The change in the modified Auger parameter $\delta$ can be considered to be an index of structural transformations involving participation of the selected chemical elements.22 For Ge, we observe an increase of this parameter, giving evidence of additional screening of the core-level electrons due to the presence of Ag in the structure. The longer the time of irradiation, the larger the Ag concentration in the matrix and the larger the value of $\delta$ (see Table I).

The chemical shift of Se 3d core-level spectrum of a Ge_{30}Se_{70} thin film to lower BE (~0.4 eV, Fig. 7) after Ag diffusion is caused by the complete disappearance of Se–Se bonds (which should be at a higher BE because of the higher electronegativity of Se atoms) and also Ge–Se–Ge fragments. The value and direction of the shift fully agree with previous data.20 Taking into
account that for the studied chemical composition the major Se 3d$_{5/2}$ component at BE = 53.8 eV should necessarily contain a Ge-Se bond, we can assume that this component is most probably associated with Se within the Ge-Se–Ag$^+$ fragments. A possible explanation for the significant (~16 at.% of Se atoms) second component at BE = 53.0 eV (for Se 3d$_{5/2}$) is Se within a covalent Ag-Se bond. The covalent origin of Ag-Se bonding was earlier predicted by appropriate ab initio band structure calculations of Ag$_2$Se.\(^\text{32}\) However, we cannot directly relate this component to phase-separated Ag$_2$Se, normally observed at a higher BE ~ 53.6 eV.\(^\text{33}\) The significant decrease of binding energy for the third component of the Se 3d core-level spectrum (51.6 eV) could be associated with lowering of oxidation number and can be assigned to onefold coordinated Se, usually expected in Se-rich ChG compositions. With increasing time of irradiation, the concentration of both minor components decreases (Fig. 8) because of structural rearrangement with the formation of an equilibrium ternary composition close to Ag$_{30}$(Ge$_{0.30}$Se$_{0.70}$)$_{70}$.

The above steps provide a detailed insight into silver photodiffusion into a Ge$_{30}$Se$_{70}$ thin film. However, a few questions still remain unclear. The most intriguing among them is the fate of the electron that becomes available as a result of ionization of an Ag atom to an Ag$^+$ ion. Photodiffusion in the present sample occurred as a result of X-ray irradiation, and we may anticipate qualitatively similar steps from exposure to lower energy photons. Yet, future experiments are planned to verify this prediction.

### IV. Conclusions

High-resolution XPS is shown to be an excellent tool for identifying the various stages of X-ray-induced silver photodiffusion into a Ge$_{30}$Se$_{70}$ thin film. By preparing a thin-film sample within the spectrometer, oxygen contamination is avoided, and evolution of radiation-induced structural changes is observed for the first time by conducting in situ measurement as a function of time. The analysis of core-level spectra indicates the formation of a Se-enriched layer consisting of Ag$_{50}$–Se$^-$ at the initial stage of silver diffusion. This layer disappears with time of irradiation. Ultimately, under equilibrium, a ternary phase based on Ge$_{30}$Se$_{50}$ units is formed, which is characterized by Ag concentration at ~30 at.%.

A separated Ag$_2$Se phase, widely described in the literature as one of the products of Ag diffusion into ChG thin films, was not detected in the present study, which was conducted completely under vacuum. The case when a ChG thin film was exposed to an O$_2$-containing atmosphere will be discussed in a future paper.

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### References


