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Conference paper

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Investigation of the oxidation process in GeTe-based phase change alloy using Ge K-edge XANES spectroscopy

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Abstract: In this work, we clearly demonstrate the efficacy of using XANES spectroscopy in conjunction with a Pilatus detector as a sensitive tool to allow the study of the oxidation process in GeTe alloys via depth profile analysis. On the basis of Ge K-edge XANES spectra, it was found that GeTe alloys do not oxidize readily after an initial native surface oxidation that occurs upon exposure to oxygen in the air at the elevated temperatures, 100 °C and 330 °C. We demonstrate that amorphous GeTe possesses a higher predisposition to oxidation than crystalline GeTe when exposed to the air at temperature of 100 °C. When the temperature is set to 330 °C in an air ambient, we show that the amorphous to crystal phase transition affects the oxidation process more significantly than the simple annealing of crystalline GeTe. We suggest that the higher tendency of GeTe films to oxidize during the phase transition is a consequence of the breaking of Ge–Ge bonds in the presence of oxygen atoms which subsequently leads to the extra formation of Ge–O bonds during crystallization.

Keywords: local structure; oxidation; phase-change memory; SSC-2018; X-ray absorption spectroscopy.

Introduction

Germanium atoms in chalcogenides have a strong tendency to interact with molecular oxygen contained in the air [1–3] and promoted by elevated temperatures or in the presence of high energy light sources [4, 5]. The Ge–O bonds are stronger and thus more stable than the Ge-chalcogen (S, Se, Te) bonds [6, 7] which inevitably leads to spontaneous and irreversible oxidation in Ge-chalcogenide materials unprotected with capping layers. In the case of GeTe-based phase-change alloys an oxygen atom bonded to a Ge atom excludes the bonded Ge atom from participation in the amorphous-crystalline phase transition and thus oxidation

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may have a strong undesirable impact on the functionality of phase change memory (PCM) devices, namely increasing the threshold voltage [8] of PCM cells which may reduce the cycleability between the SET and RESET states. On the other hand, there are some publications reporting that a small amount of oxygen incorporated in Ge–Sb–Te speeds up optically induced crystallization [9] and increases the crystallization temperature [10–13], which is important for applications of PCM in the automobile industry.

Undoubtedly, X-ray photoelectron spectroscopy (XPS) can be considered as the most common experimental method to explore the surface chemistry of a material in its “as received” state, or after some treatment, for example the oxidation process can typically be seen via a shift in the binding energy to higher energies when the oxygen atoms bond to an atom to form an oxide. Although for most applications, XPS is, in effect, a non-destructive highly sensitive surface technique, it has some experimental limitations such as requiring Ultra-high vacuum conditions and analysis is limited to the top layer to a few nanometers in depth, that simply cannot be overcome. In the case of depth profiling deeper than a few nanometers XPS must be additionally equipped with ion beam etching which turns such method inevitably to a destructive one as well. Even a mild Ar cluster bombardment is able to modify the oxidation state of a studied material [14, 15].

Unlike XPS, X-ray absorption near edge spectroscopy (XANES) in combination with a Pillatus detector can be an alternative way, and one of the few ways, how to monitor non-destructively depth profiles through 50 nm thick films with high sensitivity and nanometer scale depth resolution. The experiment can be performed at ambient conditions which is another important advantage of such set up that makes XANES even more suitable technique for depth profile analyses.

As we mentioned above, uncontrolled air oxidation may have undesirable impact on the functionality of phase change memory and may lead to the misinterpretation of results especially for ultrathin films or nanoparticles [16], where the surface plays a major role. To date, there is no comprehensive study on the depth profiles of air-induced oxidation in amorphous and crystalline Ge–Te based phase change alloys and on how phase change materials resist the oxidation process during a phase transition. To close this gap, we have collected Ge K-edge XANES spectra in natively oxidized GeTe thin films from the top layer to deep into the film to investigate how deep the air oxygen atoms penetrate into the GeTe film at elevated temperatures.

Experimental details

GeTe films were deposited at room temperature using RF magnetron sputtering onto silicon substrates. The thickness of the as-deposited films was about 50 nm. Subsequently, a part of each sample was crystallized in a furnace at 330 °C for 2 h. An inert gas (N_2) ambient was used to prevent sample oxidation. All uncapped samples were exposed to an air environment for 2 weeks to saturate the top layer. The Ge K-edge XANES depth profile measurements for as-deposited and crystalline samples at different temperatures and during their phase transitions were performed in a fluorescence mode using a Pilatus detector with 2 nm depth resolution at beam line BL01B1 at SPring-8. The acquisition time per each sample was 4 h with 5 min step between data set XANES collection. The detailed principle of the measurement has been described in the recent report [17]. Basically, when a sample is exposed by the incident X-ray beam, the fluorescence X-ray is emitted. However, the escape depth of the emitted fluorescence X-ray is limited and thus detected signals at lower angles originate only from the surface area, whereas those at higher angles come from both deeper area and the surface. The data were processed with the Athena software package using the linear combination fitting mode which allows one to obtain the contribution of XANES spectra corresponding to the Ge–Te and Ge–O bonds to the overall XANES spectrum.

Results and discussion

Fast collection of XANES from different depths is a very convenient experiment technique to discern contribution of Ge–Te and Ge–O bonds in GeTe based phase change alloys due to a shift in X-ray absorption energy of about 7 eV between Ge–Te and Ge–O bonds which allows one to monitor the Ge–O evolution. The native oxidation of the GeTe compound starts immediately when exposed to the air. Recently published results performed on single crystal GeTe cleaved under ultrahigh vacuum show that Ge atoms are oxidized in the depth of 5 nm within 2 h studied by XPS [1]. Since the surface of 50 nm thin film samples cannot be recovered to the native state before oxidation by cleaving or a surface ablation right prior to the measurement, in this work, we studied the depth profiles of natively oxidized GeTe films and the subsequent diffusion of oxygen atoms at elevated temperature rather than spontaneous surface oxidation. In our experiment, we firstly set the temperature to 100 °C in order to be able to distinguish the tendency to oxidation of both amorphous and crystalline phases to avoid the possibility of a phase transition during the experiment and in the second step the temperature was increased to 330 °C to investigate the contribution of the phase transition to the oxidation process. Figures 1 and 2 demonstrate the depth profile evolution of the Ge K XANES spectra measured for as-deposited amorphous and crystalline GeTe at 100 °C. Panels A represent depth profile XANES analyses at the beginning of measurements and panels B show depth profile XANES spectra recorded after 4 h. We would like to note that the first two collected XANES spectra from the top layer are not included in all figures due to a poor signal to noise ratio. Further, we would like to point out that the colours corresponding to the same depth are the same in all figures in the manuscript. Panels C summarize Ge–O and Ge–Te contents at

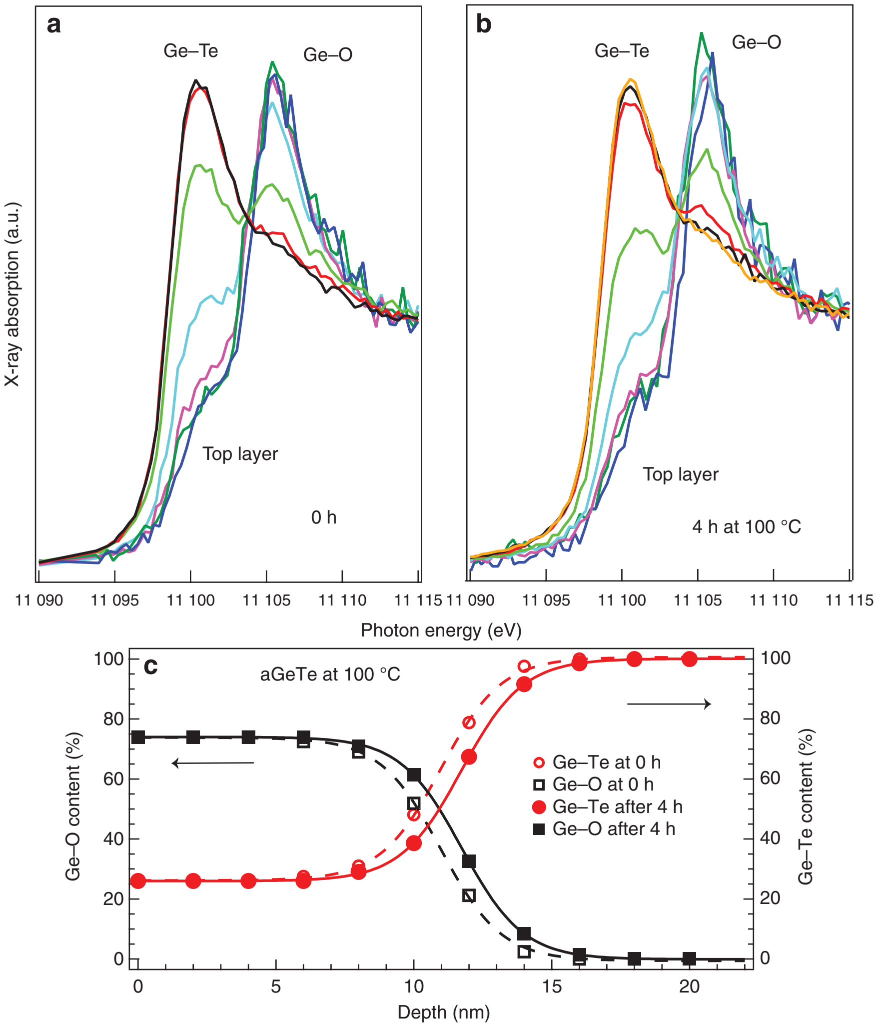

Fig. 1: Experimental depth profile evolution of Ge K XANES spectra measured for as-deposited amorphous GeTe at 100 °C in times panel (a) 0s and panel (b) 4 h. The near top layer is green and the deepest layer is black (or orange). Panel (c) represents concentrations of Ge–Te (red marks) and Ge–O (black marks) bonds in different depths.

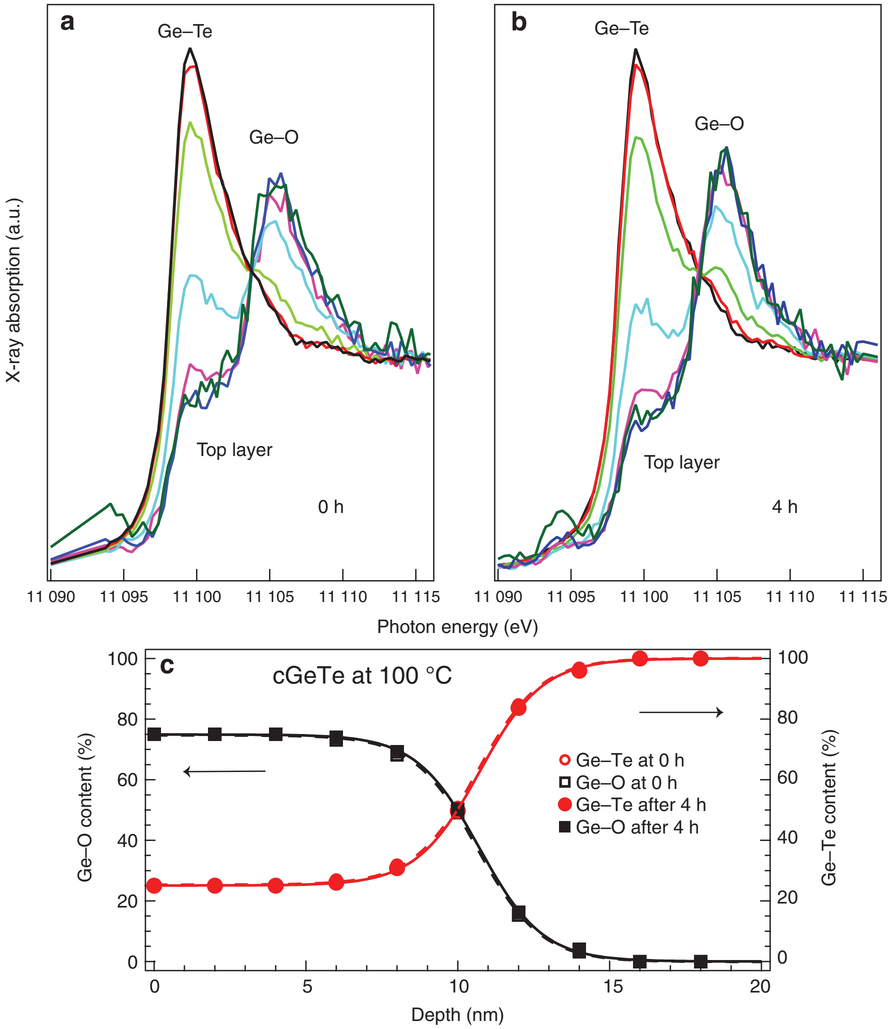

Fig. 2: Experimental depth profile evolution of Ge K XANES spectra measured for crystalline GeTe at 100 °C in times panel (a) 0s and panel (b) 4 h. The near top layer is green and the deepest layer is black. Panel (c) represents concentrations of Ge–Te (red marks) and Ge–O (black marks) bonds in different depths.

different depths after data processing with the Athena software package. One can see from the obtained data that natively oxidized top layers consist of a mixture of Ge–O and Ge–Te bonds with the constant ratio 3:1 until ≈5 nm depth followed by a transition area existing within 14–15 nm. After that only GeTe bonds can be detected.

When annealed at 100 °C for 4 h one can see that further oxidation process of the Ge atoms after the native surface spontaneous oxidation proceeds very slowly. However, we found that the start of the transition layer in amorphous GeTe moves about 1 nm deeper into the film after annealing at 100 °C for 4 h although there is little additional oxidation of the Ge atoms in the crystalline GeTe counterpart under the same conditions. We suggest that the higher predisposition of amorphous GeTe films to oxidation might result from the large number of voids [18, 19] existing in the amorphous GeTe structure which can facilitate the motion of oxygen atoms into the film that subsequently interact with the Ge atoms in deeper levels.

In order to elucidate the role of the phase transition on the oxidation process, we compared the depth profile XANES of GeTe crystallized under an inert atmosphere at 330 °C and as deposited amorphous GeTe crystallized under ambient conditions at 330 °C right before recording the experimental data. The obtained results, depicted in Fig. 3, manifest ≈1.5 nm advance of the oxidation front towards the thin film when

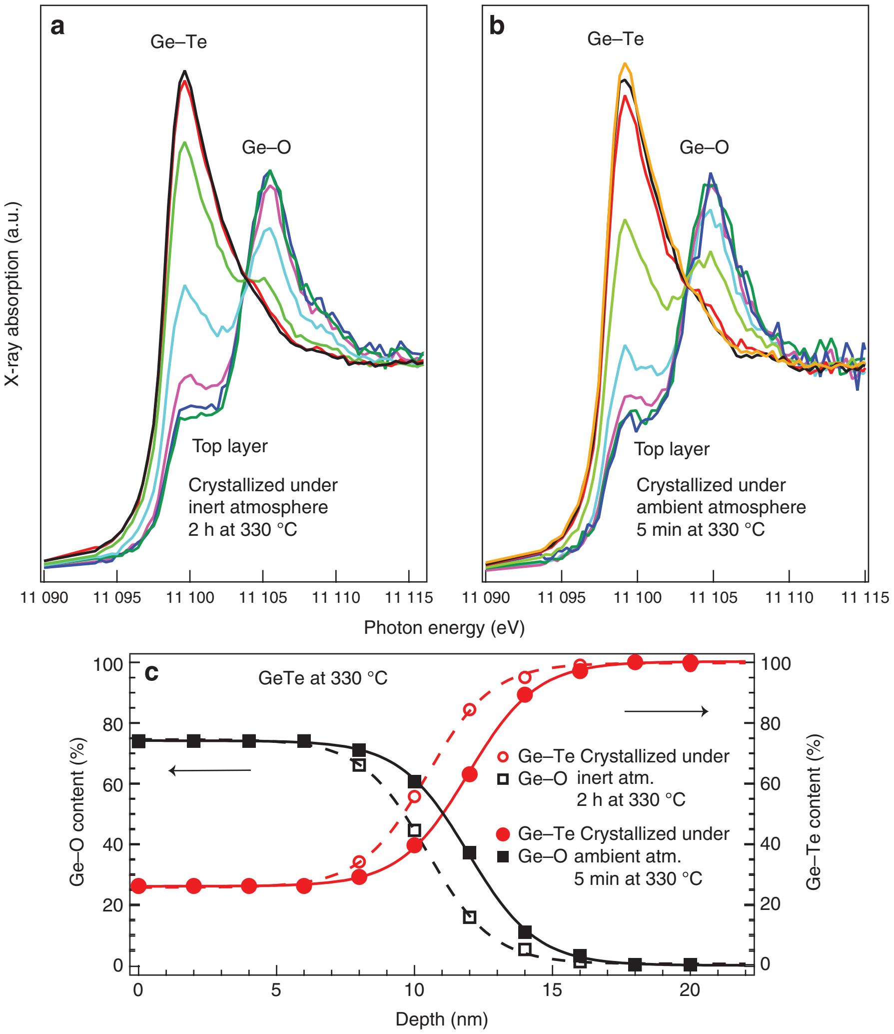

Fig. 3: Experimental depth profile evolution of Ge K XANES spectra measured for (a) crystallized GeTe at 330 °C under inert atmosphere for 2 h and subsequently exposed to the ambient conditions for 5 min. at 330 °C and (b) amorphous GeTe under ambient conditions for 5 min. at 330 °C. The near top layer is green and the deepest layer is black (orange). Panel (c) represents concentrations of Ge–Te (red marks) and Ge–O (black marks) bonds in different depths.

amorphous GeTe is transformed to the crystalline state under ambient conditions in contrast to the phase transition performed under inert atmosphere. Additional oxidation can be assigned to the change in bonding character during crystallization in combination with the higher affinity of Ge atoms to oxygen atoms than to the tellurium counterparts. More specifically, the local structure of amorphous GeTe consists of homopolar Ge–Ge bonds and heteropolar Ge–Te bonds approximately in a similar ratio. When annealed at or above the crystallization temperature, which is about 180 °C [20], Ge–Ge bonds are broken and subsequently replaced by Ge–Te bonds along with the elongation of their length and an increase in the coordination number of Ge atoms from 3.8 to 6 as reported [21, 22]. In this scenario, one may consider that breaking of Ge–Ge bonds in the presence of oxygen atoms may promote the additional formation of the Ge–O bonds during crystallization.

Finally, to determine the strength of the phase transition on the oxidation process, we collected depth profile XANES spectra of crystalline GeTe (crystallized under inert atmosphere) during long term annealing at 330 °C under air conditions displayed in Fig. 4. One can see from Figs. 3c and 4d that while crystalline GeTe barely oxidizes at 100 °C, a temperature of 330 °C stimulates the penetration of oxygen atoms into deeper levels. After 4 h annealing at 330 °C, the front of the transition layer shifts 1.5 nm into the film in comparison

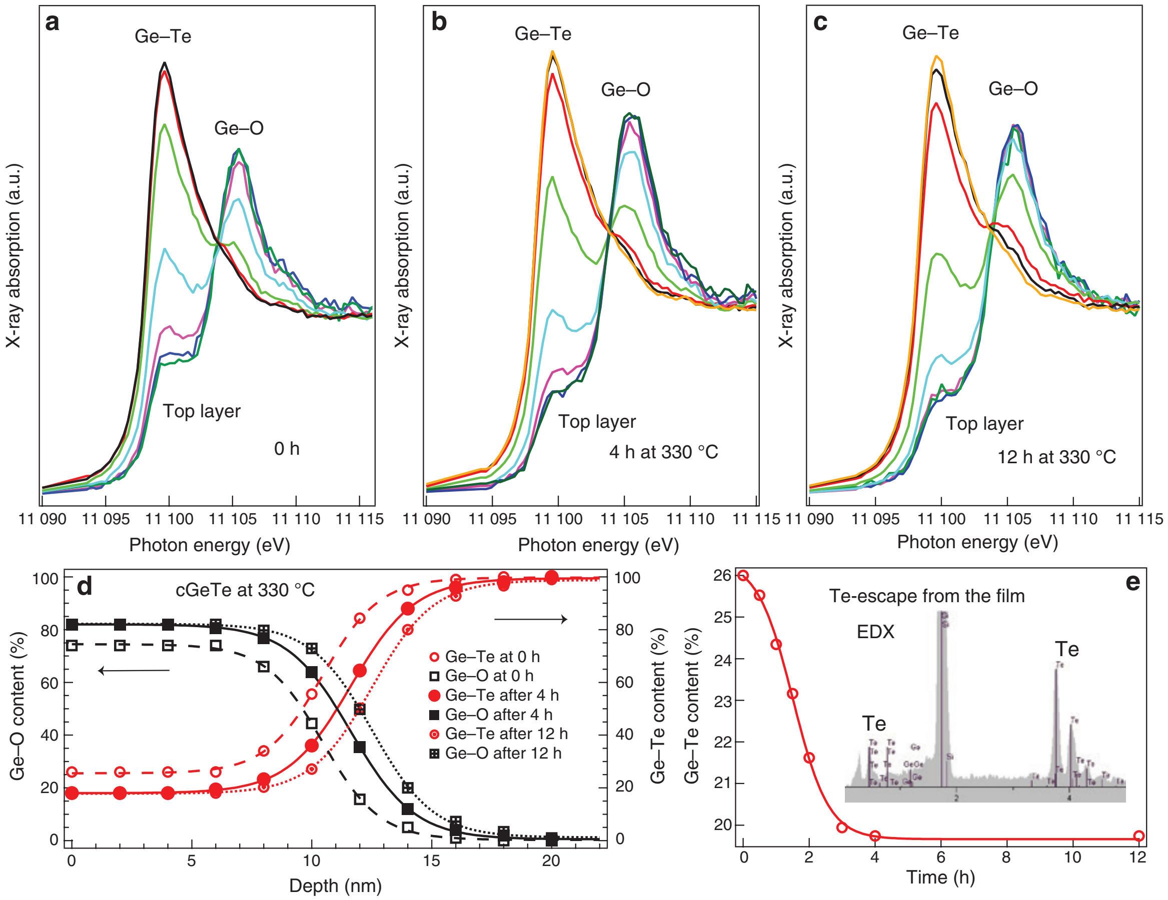

Fig. 4: Experimental depth profile evolution of Ge K XANES spectra measured for crystalline GeTe at 330 °C in times panel (a) 0 s, panel (b) 4 h (c) 12 h. The near top layer is green and the deepest layer is black. Panel (d) represents concentrations of Ge–Te (red marks) and Ge–O (black marks) bonds in different depths. Panel (e) shows the time evolution of the escape of Te content from the surface during annealing a 330 °C (inset of panel (e) is an EDX spectrum of the released material from the studied GeTe layer redeposited onto a Si wafer).

with the original state and propagates an additional 1 nm if additionally annealed for 8 h. Interestingly, the oxidative progress after 4 h is the same as that observed during crystallization which means that the phase transition affects the oxidation process more significantly than simple annealing. Nevertheless, annealing under the aforementioned conditions changes the ratio of Ge–O and Ge–Te contents in the surface layers from ≈3:1 to 4:1 which suggests that a pure Te or a Te-rich phase evaporates from the surface at this temperature. To verify the release of a compound from the surface of the film, we investigated the composition of a redeposited material onto a Si wafer mounted above the studied GeTe film sample. It was confirmed by EDX analysis that the surface is depleted by pure Tellurium as shown in Fig. 4e (inset picture) and hence Ge–Te bonds are substituted with new Ge–O bonds. It is obvious from Fig. 4e that the escape of Te atoms from the surface is gradual and the Ge–O: Ge–Te ratio becomes stable after 4 h annealing at 330 °C.

Conclusion

In summary, the experimental results presented in this work clearly demonstrate the efficacy of using XANES spectroscopy equipped with a Pilatus detector as a sensitive tool that allows the study of the oxidation process in GeTe alloys via depth profile analysis with 2 nm depth resolution. We demonstrated that the further oxidation process of the Ge atoms in GeTe after the native surface spontaneous oxidation proceeds very slowly. It has been found that amorphous GeTe possesses higher predisposition to oxidation than crystalline GeTe exposed to the temperature of 100 °C. When temperature is set to 330 °C in the air conditions, we showed that the amorphous to crystal phase transition affects the oxidation process more significantly than simple annealing of crystalline GeTe.

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