Detection of N-Te bonds in the as-deposited amorphous Nitrogen-doped GeTe-based phase change alloys using N K-edge XANES spectroscopy and their impact on crystallization.

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Abstract

Using N K-edge XANES studies, we demonstrate a noticeable difference in local structure around the nitrogen atoms in as-deposited amorphous and annealed N-doped GeTe-based phase change alloys. The pronounced changes appear as a ≈ 2 eV shift in the absorption edge to higher photon energies and the overall shape of the XANES spectrum. Comparison of the experimental XANES spectrum of the as-deposited amorphous phase with *ab-initio* XANES simulations discloses that the as-deposited phase mainly consists of the NGe_3 and the NTe_3 pyramidal units in approximately equal concentration. When annealed, NTe_3 units gradually rebond to the NGe_3 units and at the same time N atoms diffuse through the amorphous phase to form the Ge_xN_y aggregates. Upon long-standing annealing at 400 °C a compact interlayer of Ge_3N_4 is formed in the crystalline phase.

Keywords: `x-ray absorption spectroscopy`, phase-change memory, local structure

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1. Introduction

The GeTe-based alloys along the $(\mathrm{GeTe})_{\mathrm{x}} - (\mathrm{Sb_2Te_3})_{1-\mathrm{x}}$ pseudobinary tie line have become of high technological interest as phase-change materials. Their reversible and ultrafast changes between the amorphous (RESET) and the metastable cubic crystalline (SET) states on the local scale induce a large optical and electrical contrast which can be utilized in memory applications such as optical disks or electrical memory [**?** **?**]. Recent tuning of the material design along this tie line in the form of a superlattice structure significantly reduced the energy consumption necessary to switch the material between high and low resistance states as well as improved the cyclability [**?**]. However, there are some applications that require different material properties. For example, memory chips embedded in vicinity of a component irradiating a significant amount of heat, such as automobile engines, the high thermal stability of the RESET state became a top priority. One of the ways to increase the crystallization temperature,T_C of the amorphous phase is via doping of phase-change alloys by light elements such as Carbon [**?** **?**], Nitrogen [**?** **?**] or OxygenOxygen[**?** **?**]. It has been demonstrated that nitrogen incorporated into the amorphous GeTe host matrix increases T_c from 186 °C to 275 °C [**?**]. While there are several studies that attempt to investigate the origin of the increase in T_c via Bragg diffraction [**?**], x-ray photoelectron spectroscopy (XPS) or x-ray near-edge absorption (XANES) [**?** **?**] the local structure around N species which plays the crucial role in modification remains unclear.

To date, experimental [**?**] and theoretical studies [**?**] have demonstrated the presence of elemental nitrogen atoms and $\mathrm{NGe_3}$ units in as-deposited amorphous N-doped GeTe, but the existence of N-Te bonds has not been explored. In this paper, a combination of first-principle simulations and N K-edge x-ray spectroscopy is used as an effective tool to provide direct experimental evidence of the presence of the N-Te bonding ($\mathrm{NTe_3}$ structural units) in amorphous N-doped GeTe-based phase-change alloys.

2. Experimental Details

N-doped GeTe films were deposited by reactive sputtering of a GeTe target using an Ar/N_2 gas mixture onto silica substrates. The nitrogen concentration in the GeTe films was about 10 at.% which was measured by RBS (for GeTe) and Nuclear Reaction Analysis (NRA) for N. The thickness of the as-deposited films was about 100 nm. Subsequently, parts of the sample were crystallized in a furnace at 300 °C for 30 min and also for 3 h and at 400 °C for 4 h. An inert gas (N_2) ambience was used to prevent sample oxidation. In order to minimize possible composition changes due to tellurium out-diffusion at high temperatures, the samples were enclosed in a pyrex vessel containing chips of metallic tellurium to maintain a Te vapor overpressure and prevent tellurium vaporization.

The N K edge XANES measurements were carried out at BL27SU at SPring-8. The beamline is equipped with a figure-eight undulator and a Au/Si variable line spaced plane grating with a central line space of 600 lines/mm which serves as a monochromator [? ?]. The beam is sagittally focused at the sample position using a cylindrical mirror with a photon flux of approximately 2x10^{11} photons/second at the N K-edge and a resolving power of E/E of approximately 2500. For the current experiments, integer-order harmonics from the undulator were used resulting in a horizontal (in-plane) polarization for the grazing incidence geometry used. The photon energy resolution was 80 meV.

2.1. Structure modeling and XANES calculation

To be able to discern the contributions of the various structural units present in the experimentally observed XANES spectra, we performed XANES calculations using several N-doped GeTe prototypical models containing 55 atoms. Bearing in mind the condition that Ge atoms predominantly form tetrahedral units in many materials such as pure germanium [?], Ge-S (Se) [?] and as-deposited amorphous GeTe [?], a model structure can be easily obtained using GeTe in a zinc-blende modification (ZBM) as a starting point. Next, the coordination numbers for Ge-Ge, Ge-N and Ge-Te bonds were adjusted to match the experimental values obtained from EXAFS measurement on samples with the same composition [?]. To investigate the effect of N-Te bonds we gradually replaced Ge-N bonds by N-Te bonds. The density of Ge-Te alloys (ZBM) was reduced by removing several atoms to realize the experimental density of GeTe to be 5.4 g/cm^3 keeping in mind the coordination numbers and tetrahedral ordering of Ge atoms [?]. At the same time, the deletion of several atoms served to disrupt the long range ordering that helped to collapse of the prepared crystalline model into amorphous counterpart studied here. The prototypical amorphous models of the N-doped GeTe based alloys were obtained by relaxation of the above modified Ge-Te ZBM structures via density functional calculations using the plane wave code CASTEP [?]. Ultrasoft pseudopotentials and the local density approximation (LDA) for the exchange potential were used. The LDA term was formulated from the numerical results of Ceperley and Alder [?] as parameterized by Perdew and Zunger [?]. The charge density was calculated with a plane wave cutoff of 220 eV and a $2 \times 2 \times 2$ Monkhorst Pack grid [?]. For the relaxation processes, the Broyden, Fletcher, Goldfarb and Shannon algorithm [?] was used to relax the atomic coordinates at 0 K within a supercell of fixed volume; the volume was fixed to reflect the experimental determined density, as is conventionally done in the literature [?]. Subsequent annealing of the amorphous N-doped GeTe model was carried out at 700 K using a $2 \times 2 \times 2$ k-point mesh, the nose thermostat and NVT conditions. The total computation time was 200 ps with 3 fs steps.

The theoretical XANES spectra were calculated using the ab-initio real-space full multiple-scattering code FEFF9 [?] via relaxed prototypical models of amorphous and annealed GeTe-based alloys. FEFF9 is a fully relativistic, all-electron Green function code that utilizes a Barth-Hedin formulation for the exchange-correlation part of the potential and the Hedin-Lundqvist self-energy correction. In our FEFF calculations, the cluster radius was set to 9 Å around the central atom, which corresponds to about 100 atoms in the model. XANES spectra were calculated for each nitrogen atom in the unit cell. Representative XANES spectra for each structural unit were obtained by averaging of at least three different XANES spectra of the same local environment around the nitrogen atoms.

3. Results and Discussion

Figure 1 shows experimental N K-edge XANES spectra of N-doped GeTe in as-deposited and thermally-crystallized states. Examination of the N K-edge XANES spectra reveals a pronounced difference between the spectra in the form of a 2 eV shift in the absorption edge to higher energies (photon energy from 398 to 400 eV) and the overall shape of the XANES spectra. From Fig. 1, one can see that by annealing of the as-deposited film, the intensity of the feature in the range of energies from 398 to 400 eV gradually decreases together with a monotonic shift of the absorption edge with increasing annealing time. In addition, a band at 403 eV significantly increases in intensity and further annealing leads to form an additional peak at 404.5 eV. All observed changes in the XANES spectra indicate a change in the local environment around nitrogen atoms during the phase transition.

Firstly, we focus on the interpretation of the as-deposited amorphous N-doped GeTe phase. Recent results in the literature suggest that nitrogen atoms are exclusively surrounded by Ge atoms in the form of NGe_3 pyramidal and a few NGe_4 tetrahedral units and may partially segregate into Ge_xN_y [**?**]. Using the hypothesis, a prototypical N-doped GeTe model was generated where all nitrogen atoms were three-fold coordinated by germanium atoms. After relaxing the model to its minimal energy structure using CASTEP, N K-edge XANES spectra were calculated for each N atom site in our ”Melt-quenched-like” model of N-doped GeTe using the ab-initio real-space full multiple-scattering code FEFF9 and subsequently averaged. Strikingly, the resulting XANES spectrum of the ”melt-quenched-like” model of N-doped GeTe appeared a better match to

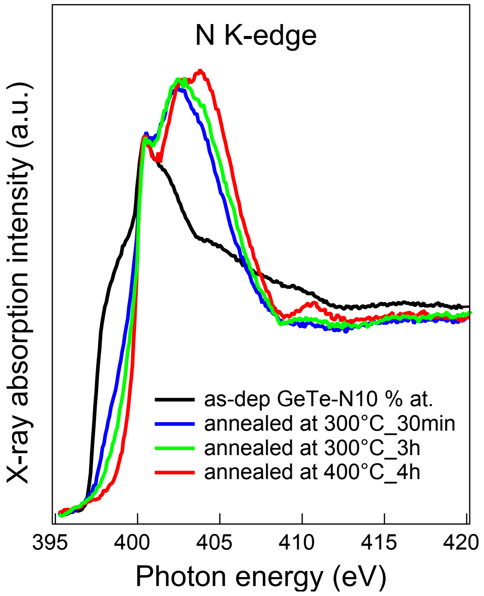

Figure 1: (Color online) Experimental N K-edge XANES spectra of amorphous and annealed N-doped GeTe which demonstrate a significant difference in the local environment of nitrogen atoms during the phase transition.

the experimentally obtained XANES spectrum for the crystalline state rather than to that of the as-deposited amorphous counterpart (see Fig. 2 NGe_3 units red curve and as-deposited N-doped GeTe brown dashed curve). Namely, the absorption edge was situated at 399.7 eV and the spectrum was peaking at 403.8 eV the melt-quenched-like model while the as-deposited amorphous phase began to absorb at 398 eV and the maximum intensity of the XANES spectrum was at 400 eV.

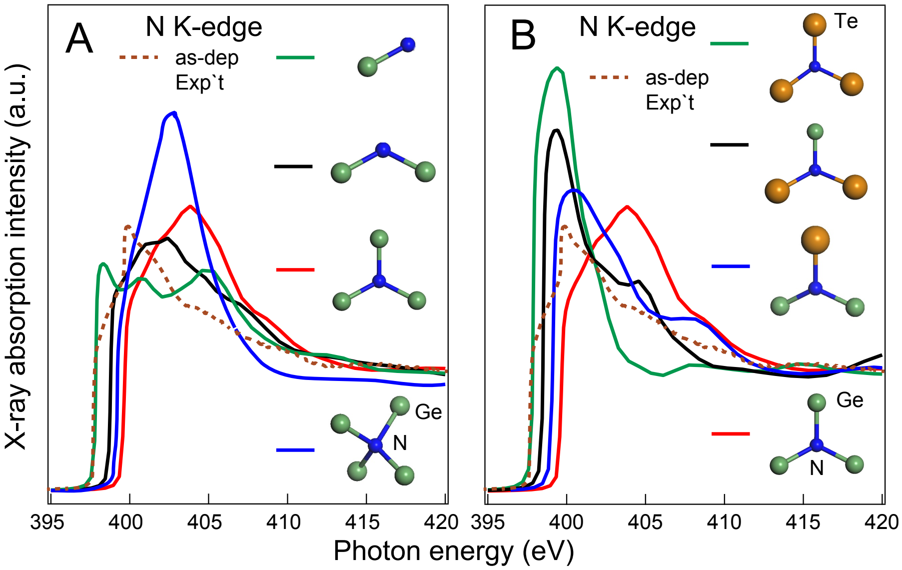

Figure 2: (Color online) Calculated N K-edge XANES spectra for A) NGe_4, NGe_3, NGe_2 and NGe fragments, B) NTe_3, NTe_2Ge, $NTeGe_2$ and NGe_3 units. Note, NGe_4 is formed during annealing in Ge-rich areas and one-fold coordinated N-Ge was artificially generated since it is unstable during atomic optimization at 0 K. The dashed brown curve represents the experimental XANES spectrum for the as-deposited amorphous N-doped GeTe phase.

Since the NGe_3 pyramids randomly distributed in the amorphous phase do not describe the N K-edge XANES spectrum of the as-deposited amorphous N-doped GeTe phase, two possible scenarios can be considered, namely the presence of N-Ge fragments, where N is less than three-fold coordinated and secondly additional N-Te bonds formation as recently demonstrated in [**? ?**].

In order to study the effect of both N-Te bonding and N-Ge fragments, sev-

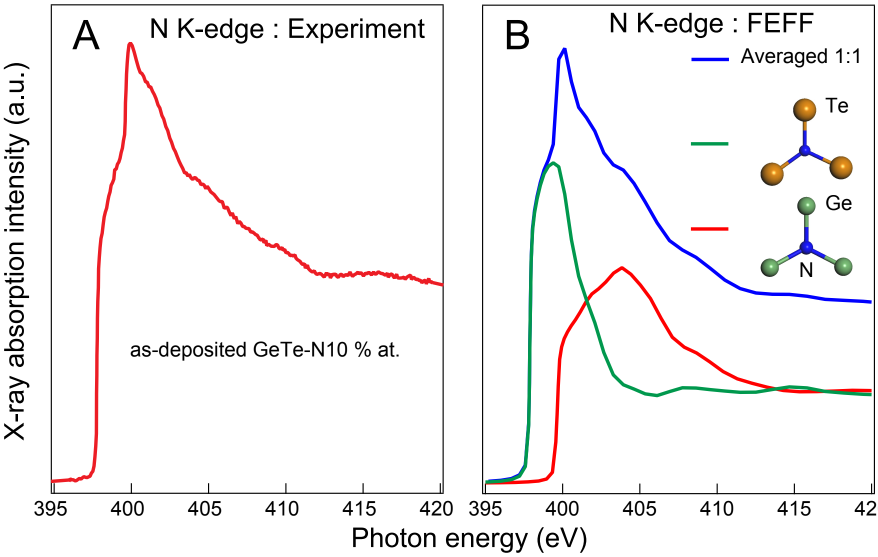

Figure 3: (Color online) N K-edge XANES spectra for as-deposited amorphous N-doped GeTe: experiment (left panel) and simulated using FEFF9 (right panel). The simulated averaged N K-edge XANES spectrum shows obvious contributions from two main structural units, namely NTe_3 (green) and NGe_3 (red) pyramidal units approximately in the equal concentration.

eral new models were generated containing NTe_xGe_{3-x} pyramidal units with different Ge and Te ratios and then subsequently relaxed in CASTEP. Amazingly, it was found in our prototypical models that only two of 50 nitrogen atoms possessed NGe_2 surroundings which may indicate that the formation of such fragments may be energetically unfavorable. Even for these cases, the nitrogen atoms were three-fold coordinated but one of the atoms (usually N) was located about 0.5 Å beyond the bond length cut-off which was set to be 2.2 Å. The simulated N K-edge XANES spectrum corresponding to the NGe_2 unit (see Fig. 2 A) significantly changed its shape with a maximum intensity at 402.4 eV however the position of the absorption edge was located at about 398.9 eV which is still quite distinct from the experimental value 397.8 eV. To complete the scenario of N-Ge fragments, a structure with one-fold coordinated N atom was artificially constructed although it is necessary to emphasize that this fragment is unstable and rapidly rebonds to NGe_3 during atomic optimization at 0 K. However, the simulated N K-edge XANES spectra for the latter unit shows the position of the absorption edge in the right place at 397.8 eV but the intensity of the white-line is low and the whole XANES main feature is too wide which has the consequence that any combination of N-Ge fragments alone did not lead to the reproduction of the experimental XANES spectrum properly.

Next, we consider possible contributions from species containing N-Te bonds. The calculated N K-edge XANES spectra for corresponding groups of NTe_3, NTe_2Ge, $NTeGe_2$ can be seen in Fig. 2 B. One can clearly see from the Fig 2 B a gradual shift in the absorption edge towards lower photon energy together with a progressive increase of the so-called "white-line" from NGe_3 to NTe_3 pyramids. Interestingly, the absorption edge of the NTe_3 unit can be found at 397.8 eV which is the exact position of the absorption edge for the as-deposited amorphous N-doped GeTe. On top of thus, a combination of XANES spectra for NGe_3 and NTe_3 in a 1:1 ratio nearly perfectly reproduces the overall shape of the experimental XANES spectrum of the as-deposited amorphous N-doped GeTe (see Fig. 3 B). One can see that the absorption edge and peak positions at 399.7 eV, 401 eV, 404 eV, 409 eV and 415 eV correspond well with the experimental data. Strong similarities between the two spectra allow us to draw the conclusion that the newly observed NTe_3 pyramids together with NGe_3 pyramids should comprise the dominant structural units on the local scale in the as deposited N-doped GeTe. It is fair to stress that there may be a contribution from the elemental nitrogen which can be found at 400 eV [**? ?**].

As mentioned above, annealing of the as-deposited amorphous N-doped GeTe significantly modifies the local structure around the nitrogen atoms. Fig. 4 (upper panel) represents the evolution of the simulated XANES spectra for the as-deposited amorphous N-doped GeTe model containing the NTe_3 and NGe_3 units when annealed at 700K from 0 (A) to 200 ps (D) using ab-initio molecular dynamics. It is obvious from structural models A to D (Fig. 4 bottom panel) that by annealing the NTe_3 units gradually bond to the NGe_3 units and at the same time the nitrogen atoms diffuse through the amorphous phase to form the Ge_xN_y agglomeration which is manifested by the model E. The replacement of the Te atoms by the Ge atoms in the NTe_3 pyramids has a strong impact on the edge jump intensity connected with the shift of the absorption edge to higher photon energies and on the progressive evolution of the peak at 403 eV corresponding to the N-Ge bonding. The observed trend in the XANES development is in a very good agreement with the experimental results shown in Fig. 1 which suggests that the NTe_3 pyramids are responsible for the 2 eV shift in the absorption edge between the as-deposited and annealed N-doped GeTe. We also note that since the N-Te bonds are likely to decompose they could become the source for creation of molecular nitrogen in the crystalline GeTe-based phase change alloys [**? ?**].

Of special interest is a new intense feature at 404.5 eV that emerges in the sample annealed at 400 °C for 4 hours. Recent experiment on crystallized N-doped GeTe [**?**] reported that during crystallization the originally homogeneous as-deposited amorphous phase segregates such that small crystalline grains of GeTe become encapsulated by a germanium nitride phase. The existence of the latter phase served as motivation to simulate the XANES spectrum for pure Ge_3N_4 and compare it to the experimental XANES spectrum of a sample an-

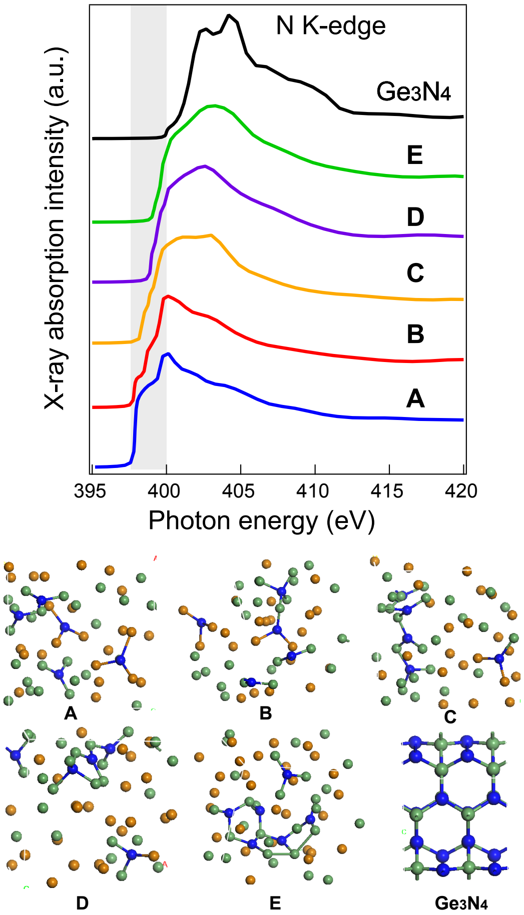

Figure 4: (Color online) The evolution of simulated XANES spectra during annealing of the as deposited amorphous N-doped GeTe model (A) at 700 K from 0 to 200 ps (D) with different concentration of the N-Te bonds, the model (E) illustrates annealed a melt-quenched N-doped GeTe with organized Ge_xN_y inclusion and compared with the Ge_3N_4 phase. The representative models are displayed under the calculated XANES spectra where green, blue and gold spheres represent Ge, N and Te, respectively. Only bonds within N-Ge and N-Te clusters are indicated other bonds are not shown. Bond length cut-offs of 2 Å and 2.2 Å were used for N-Ge and N-Te bonds, respectively.

nealed at 400 °C for 4 hours. Strikingly, except for the peak located at 403 eV one can see a second intensive band at 404.5 eV in the simulated XANES spectrum which perfectly agrees with the new feature on the experimental curve. Therefore it is possible to conclude that a compact interlayer of Ge_3N_4 is formed in the crystalline phase after extended annealing at 400 °C. In addition, looking carefully at the XANES spectrum for Ge_3N_4 one can see that the absorption edge shifts to 402 eV while the position of the absorption edge for annealed N-doped GeTe remains at 399.7 eV. This edge energy difference may be a result of both the absorption edge of the molecular nitrogen contained within crystalline grains and NGe_3 pyramidal units or their small inclusion incorporated separately into the crystalline lattice. The XANES spectra for the latter phases are demonstrated in Fig 5.

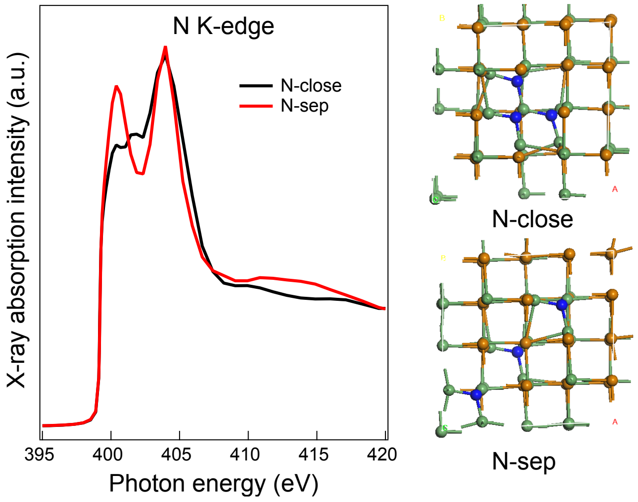

Figure 5: (Color online) N K-edge XANES spectra simulated for differently distributed nitrogen atoms which occupy tellurium positions in the crystalline matrix of GeTe. The red curve represents the simulated average XANES spectrum for three nitrogen atoms well separated from each other while the black curve is the simulated average XANES spectrum for three nitrogen atoms interconnected via one germanium atom. The representative models are displayed on the right side where green, blue and gold spheres represent Ge, N and Te, respectively.

Fig. 5 shows additional pronounced dissimilarity in the N K-edge XANES spectra depending on the way N atoms are incorporated into GeTe host matrix. When a nitrogen atom occupies a tellurium site in the crystalline GeTe host matrix and at the same time does not share all three germanium atoms with another nitrogen (see Fig. 5 N-sep), a strong peak at 401 eV can be seen in the simulated N K-edge XANES spectrum. In contrast, while N atoms are linked via the germanium atoms to form an inclusion within the GeTe matrix (see Fig. 5 N-close) the peak splits into two low intensity peaks centered at 401 and 402 eV. Such difference could provide information about content of these two local environments. In comparison with experimental XANES spectra for the annealed phases, there is no strong peak at 401 eV which is also a maximum attributed to the white-line of the N_2 molecules [**?**] and the main band peaking at 403 eV is wide and gradually increases the intensity from 401 eV. Hence we assume that Ge-N segregation is the dominant process during crystallization; the contribution of nonsegregated NGe_3 to the local environment embedded into crystalline GeTe appears to be small.

By an analysis of N K-edge XANES spectra we efficaciously determined the existence of specific nitrogen sites in phase-change materials which may influence material properties such as crystallization temperature. Crystallization of as-deposited N-doped GeTe seems to be connected with the disassociation of the NTe_3 pyramids, diffusion of the nitrogen atoms through the material via NTe_xGe_y fragments and the NGe_3 units to form segregated Ge_3N_4 at the edge of GeTe grains. Subsequent amorphization by laser or electric pulses may not transform the crystalline material into the original state. The Ge_3N_4 phase could be preserved in its crystalline state due to its high melting temperature which is about 900 °C [**?**] and thus the contribution of the nitrogen atoms to the subsequent crystallization cycles may decrease which may reduce the crystallization temperature to that of pure GeTe. Since germanium nitrogen bonding is preferential, only a small amount of nitrogen should be used to tune material properties in order not to strongly modify the composition of the phase change alloys after cycling and initiate further segregation. A similar trend could be expected in cases when the phase change material is doped by other light elements such as oxygen or carbon.

4. Conclusion

In summary, the experimental and theoretical results presented in this work demonstrate the efficacy of using N K-edge XANES spectroscopy as a sensitive tool that allows one to detect the presence of NGe_3 and NTe_3 local bonding geometries in as-deposited nitrogen doped GeTe-based alloys. We demonstrated that by annealing, NTe_3 units gradually transform to NGe_3 via NTe_xGe_y fragments and finally segregate as Ge_3N_4. We also found that a compact interlayer of Ge_3N_4 is formed in the crystalline phase upon long-standing annealing at 400 °C.

5. Acknowledgment

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