Rijksuniversiteit Groningen

Bachelor Thesis

Simulating scanning transmission electron microscopy images of GeTe-Sb_2Te_3 superlattice structures

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Abstract

A new type of phase change materials based on Ge, Sb and Te is under large investigation for memory applications. This new nanostructured concept based on GeTe-Sb_2Te_3 superlattices shows better magnetic and electrical properties compared to their bulk counterparts. The research of Momand et al. in 2015 with high-angle annular dark field scanning transmission electron microscopy gave more information about the structure of the created GeSbTe blocks. However, the resulting images and intensity functions were not compared to theoretical calculations yet. In this work, the structure of these GeSbTe blocks is further examined using computer simulations. The annealed $GeSb_2Te_4$ tends to have a 65-30-90 composition on the sequential cation layers, where the annealed $Ge_2Sb_2Te_5$ blocks shows signs of a symmetric 65-35 composition on the sequential cation layers. Furthermore, the results show that the computer simulations are not as accurate as initially thought due to approximations in the software. According to the simulations, the way of normalizing applied by Momand et al. is not recommended and a non-local normalization is preferred. Overall, the simulation software is a valuable method to give extra conclusions on the atomic layers in materials but a few improvements have to be made.

Introduction

Phase change memory is a nonvolatile solid state memory technology that is build around the large difference in electrical properties of the amorphous and crystalline state of some specific materials [1]. Recently, a new concept of phase change materials (PCMs) has been developed which is based on alternating blocks of GeTe and Sb_2Te_3 and is referred to as Chalcogenide Superlattice (CSL) [2]. This new nanostructured material is seen as one of the most promising candidates for next-generation data-storage [2, 3]. The material has better switching properties and brings new possibilities for switching between multiple levels [4]. On top of that, in the GeTe-Sb_2Te_3 superlattice it is also possible to induce a extraordinary high magnetoresistance [5]. This means it is maybe possible to create new memory devices that uses both phase change and magnetic memory. Despite the advantages of CSL, the crystal structure of the material is currently not completely understood [6]. In 2015, Momand et al. [6] shed new light on the interface formation between GeTe and Sb_2Te_3. GeTe-Sb_2Te_3 superlattices were grown on a silicon substrate and then investigated using high angle annular dark field scanning transmission electron microscopy (HAADF-STEM). These results helped to give a better understanding of the crystal structure of the CSL's and the way GeSbTe blocks are created, but were not compared to theoretical calculations yet. In the present work, HAADF-STEM imaging is simulated using the software package dr. Probe [7]. These images are compared to the experimental data of ref. [6]. In this way, the structure of the annealed CSL, consisting of blocks $GeSb_2Te_4$ and $Ge_2Sb_2Te_5$, can be further examined. If accurate enough, this method can give conclusions on the amount of mixing between Ge and Sb in the 7 and 9-layered structure. By performing extra simulations, also more information can be gathered about the working of HAADF-STEM imaging. It is tested whether the thickness of a sample plays an important role, along with the influence of vacancies in the crystal lattice. From all these results it will be concluded if the software package dr. Probe is a valuable method for comparing experimental HAADF-STEM images to computer simulations and really give information about the crystal structure of the examined materials.

Theory

Multiple models have been proposed for the structure of GeTe-Sb_2Te_3 superlattices [6, 8]. Both GeTe and Sb_2Te_3 are based on abc-stacking of close-packed atomic planes [6]. When growing GeTe-Sb_2Te_3 superlattices, different GeSbTe-blocks are formed. The blocks consist of Sb_2Te_3 with multiple units Ge-Te- intercalated, which results in 5, 7, 9, 11 or 13-layered structures. Between the blocks are Te-Te bonds which are of the van der Waals type. Therefore the structure is called a van der Waals (vdW) heterostructure. The GeSbTe layers are formed due to the difference in bonding dimensionality of bulk GeTe and Sb_2Te_3 [6]. Bulk GeTe prefers 3D-bonding [9] and is

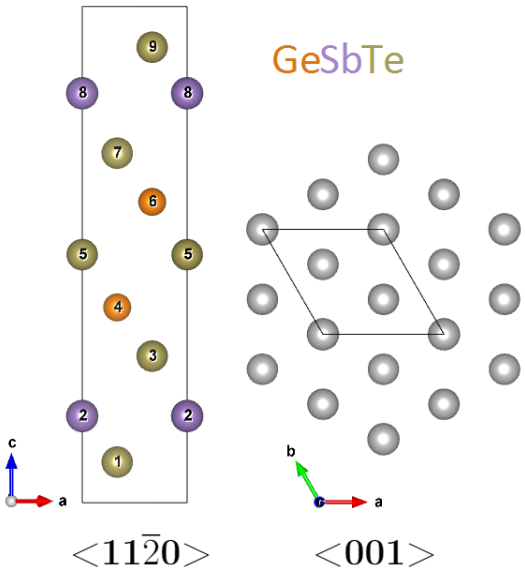

Figure 1: Crystal structure of $Ge_2Sb_2Te_5$ proposed by Kooi et al. [8].

therefore more likely to be bonded within the 2D-bonded [10] Sb_2Te_3 block, instead of adjacent to the van der Waals gap. This results in a stacking sequence of Te-Sb-Te-(Ge-Te-)$_n$Sb-Te- for $n = 0$, 1, 2, 3 or 4, which is shown in figure 1 for the 9-layered variant. This structure was proposed by Kooi et al. [8] in 2002 and fits experimentally best with the stable phase of $Ge_2Sb_2Te_5$, where pure Ge and Sb layers are assumed. The research of Momand et al. showed that the structure of the superlattice changes after annealing the sample for 30 minutes at 400 °C. Instead of a sequence of 5-, 7-, 9-, 11-, and even 13-layered blocks, only a vdW heterostructure with 7- and 9-layered blocks is left. Furthermore, before and after annealing the sample, all the GeSbTe blocks show intermixing of Ge and Sb on the cation sublattice, where the Te atoms fully occupy the anion sublattice. In the [11$\bar{2}$0] viewing direction we see, apart from the adjacent Te-Te van-der-Waals bonds, always alternating cation and anion planes as a function of the distance to the interfaces (and the vdW gaps which are parallel to the interface). The cation layers are not pure Ge or Sb, but are a mix of both. The outer cation layers most close to the vdW gaps (first assumed to be pure Sb) still consist of more Sb than Ge, where the inner cation layers consist of more Ge. Earlier research also observed this phenomena [11]. In that research, the occupancy of atoms in the different layers show symmetry: the outer cation layers 2 and 8 have the same occupancies, even as the inner cation layers 4 and 6.

The CSL's blocked structure is investigated using high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM). In annular dark field imaging, the images are formed by collecting the scattered electrons with a annular dark field detector [12]. If this image is only formed by the very high-angle, incoherently scattered electrons, the image is extremely sensitive to the atomic number Z of the atoms. Because of this Z-dependence, HAADF-STEM is an helpful tool to see the difference between the different atoms in a sample and therefore give more information about the crystal structure. According to ref. [13] the average intensity of an image can be calculated from

$$\frac{I_{av}}{I_0} = \beta Z^2$$

where I_0 is the minimal intensity and β is a variable dependent on multiple factors, including the radius of the atoms. The atomic radius is again proportional to the atomic number, resulting in a Z-dependence that is always lower than 2. Therefore the intensity of HAADF-STEM images is proportional to Z^α, where different values for α are found between 1.2 and 2 [14–16] and the average is approx. 1.8. The structures are observed in the [11$\bar{2}$0] direction. This direction is used to keep the interface edge-on such that the closed packed atomic planes can be observed best. This also provides the largest spacing between atomic columns parallel to the interface, resulting in the best atomic resolution.

For performing simulations on HAADF-STEM imaging, the software package Dr. Probe is used [7]. Dr. Probe is a tool package for multi-slice image simulation in high-resolution scanning and imaging transmission electron microscopy. The software simulates an STEM image at a set thickness based on multiple slices along the thickness direction. For this, a crystal structure has to be imported and multiple microscope settings have to be filled in. The simulations are based on the frozen lattice (FL) approximation. In the frozen lattice model, multiple lattices are created where the atoms are randomly displaced each time based on the thermal displacement parameters. This is a reasonable approach, because the crystal lattice appears stationary for an incident electron since the interaction time with the lattice is much shorter than the vibration period of the atom in the crystal [17]. The STEM image is simulated for all these different lattices and then the intensity of the different images is averaged.

In the present work, it is tried to give more information on the amount of mixing between Ge and Sb in the cation layers by comparing the simulations of dr. Probe with the experimental data of ref. [6].

Experimental

The parameters for the microscope in Dr. Probe are based on the STEM used in ref. [6]. The STEM has an accelerating voltage of 200 kV, the semi-converging angle is 22 mrad and the collecting angles are 68-280 mrad. The images were simulated with 20 variants of the FL approximation and a sampling rate of 0.01 nm per pixel. Only the middle part of all the images is used to rule out possible edge effects. This results in images of 73x173 and 74x208 pixels for $Ge_2Sb_2Te_5$ and $GeSb_2Te_4$ respectively. Images are convoluted using a Gaussian distribution with a half-width

half-maximum (HWHM) of 0.04 nm. All intensity line scans except figure 5 and 6 are averaged over 73 or 74 pixels and normalized in the same way as in ref. [6]: by dividing them with a highest order unique polynomial through the Te peaks in the GeSbTe blocks. The simulations are computationally heavy. Simulating an HAADF-STEM image in dr. Probe typically takes approximately 4 hours using a Intel i7 CPU and 8 gigabytes of memory.

All structure files are created with the freely available VESTA Crystallography software [18], which can export structures as a format that is compatible with Dr. Probe (.cif files). The structural parameters, including lattice constants, atom coordinates and thermal displacement parameters of $GeSb_2Te_4$ and $Ge_2Sb_2Te_5$ are found in literature [19, 20], where these parameters have been determined using X-ray diffraction. The structures in figure 1 are also visualized using VESTA. Because the software package dr. Probe is relatively unknown, the working of this program is tested by performing simulations on the examples found in ref. [7]. Because the simulations with the methodology of the present work gave the same results as in the examples, it is concluded that the software is used correctly.

Results

An important parameter of the simulations is the thickness of the sample in the viewing direction $[11\bar{2}0]$. In the research of ref. [6], the thickness of the specimen is unknown because it was not constant[1] and hard to measure. Therefore, the simulations are first tested on thickness dependency to decide what is a reasonable thickness for the simulations. As discussed earlier, dr. Probe creates multiple slices along the $[11\bar{2}0]$ direction. The software features an option to read out the images at every slice, instead of only once at the end. These images are used to plot the intensity as a function of the height for different thicknesses. Earlier research proposed that in these graphs the ratio between the intensity of Te and Ge or Sb peaks should be constant, because the intensity of an HAADF-STEM image should scale with Z^α, where Z is the atomic number [14–16]. Therefore, the ratio can be calculated from $\frac{I_1}{I_2} = (\frac{Z_1}{Z_2})^\alpha$, where I is the intensity and the indices are representing different intensity peaks. The simulations on thickness dependency are performed on two samples. First a sample of $Ge_2Sb_2Te_5$ is used with pure Ge and Sb layers, so the occupancy of the atoms along the thickness does not play a role. The results are shown in figure 2a. The ratio is not constant for small thicknesses. When the sample is thick enough ($d > 5$ nm), two ratios in the first sample (layers 1-2 and 8-9) are in good agreement with the Z-dependence of $\alpha = 1.8$. The other ratios do not match the proposed Z-contrast, but are almost constant after thickness $d = 20$ nm. Therefore, all the following simulations in this research are performed on samples with a thickness of at least 20 nm. The ratios of layers 3-4 and layers 6-7 do not match the Z-dependence, maybe due to the fact that the atoms are relatively close. If the intensity distributions would overlap, this

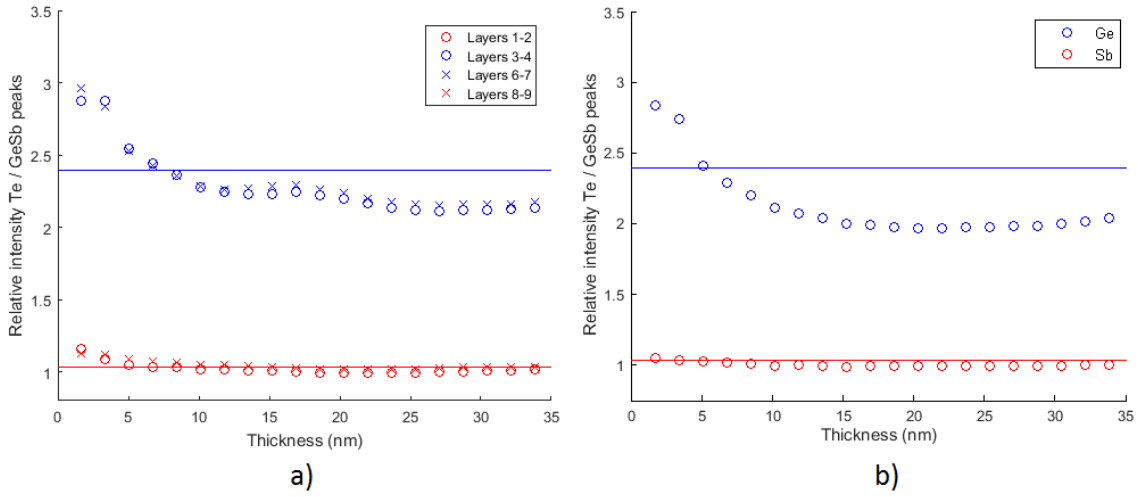

Figure 2: Ratios of the intensities as a function of the thickness with pure Ge and Sb layers in a) $Ge_2Sb_2Te_5$ samples and b) samples with the atoms far away from each other. The horizontal lines correspond to the Z-contrast of $\alpha = 1.8$.

[1]The specimen is prepared with a sharp wedge and therefore has varying thickness along the sample.

would directly influence the ratios. To examine this, a second sample with a Ge, Sb and Te atom further away from each other (1 nm) is simulated on different thicknesses. The results are shown in figure 2b. The ratios follow the same trend as in the $Ge_2Sb_2Te_5$ sample, from which it can be concluded that the atomic distances do not play an important role. Based on the simulations with the second sample, the intensity of HAADF-STEM imaging rather scales with $\alpha = 1.4$ instead of the averaged value $\alpha = 1.8$.

$Ge_2Sb_2Te_5$

The HAADF-STEM images of Momand et al. on annealed blocks of $Ge_2Sb_2Te_5$ are compared with simulations in dr. Probe. In this way it is tried to determine the occupancies of Ge and Sb in layers 2, 4, 6 and 8. On first guess, based on the intensity line graph of the experimental data, a symmetric sample with 33% Ge and 67% Sb in the outer layers and 67% Ge and 33% Sb in the inner layers is simulated. This is from now on called the 33-67 composition, referring to the occupancy of Sb in the inner and outer layer respectively. The result is shown in figure 3, along with the normalized experimental data. The simulations are already close to the experimental data. Multiple new samples are created with small deviating occupancies to look at the differences in intensities and see which fits the experiments best. The results are shown in figure 9 in the appendix. For clarity, only the Ge/Sb peaks of the simulations are plotted there. The Te peaks always match perfectly due to the way of normalizing. The simulations showed that for the different layers different compositions are favored. For the second layer the 37-63 composition is closest, where in layer 6 the 32-68 composition is closest and 33-67 is favored in the eighth layer. For the fourth layer the simulations don't seem to match the experimental peak at first sight, but the differences are small and because the peak is very sharp and has larger fluctuations (maybe due to experimental error) it is possible that the real maximum is above the line graph. Overall the differences in composition do not seem to follow a Z-dependency perfectly. For example in layer 2, where the 37-63 composition shows higher intensities than the 35-65 and 32-68 compositions, but the latter two have higher atomic number. This is probably due to the randomizations the software performs for the frozen lattice approximation (examined in extra simulations) and the way of normalizing, resulting in error margins for every simulation. Therefore performing simulations with occupancy changes in the order of 1% is not fully legitimized, because the simulations do not have that accuracy. According to these simulations, the best fitting composition of annealed $Ge_2Sb_2Te_5$ is 65±3% Sb with 35±3% Ge in outer layers 2 and 8 and 35±3% Sb with 65±3% Ge in inner layers 4 and 6.

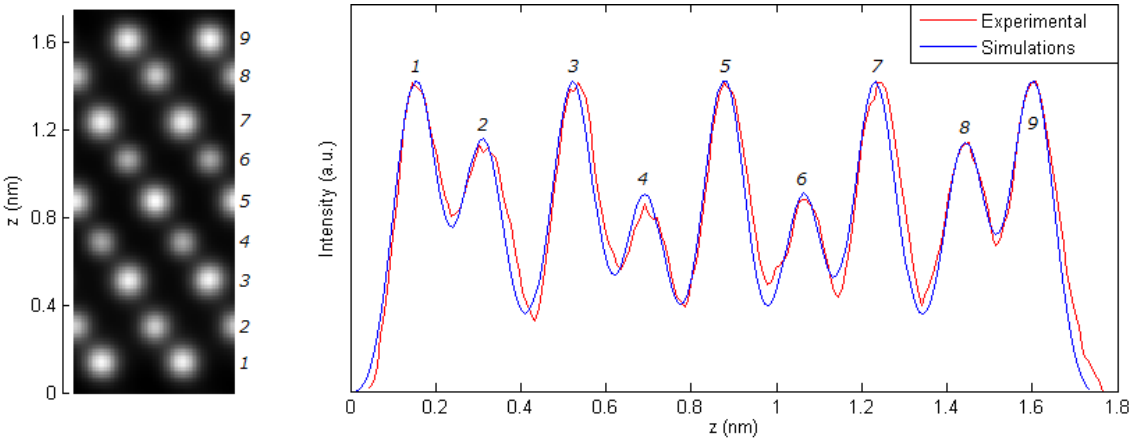

Figure 3: Results of simulating $Ge_2Sb_2Te_5$ in dr. Probe with 33-67 composition. On the left the convoluted image exported by the software and on the right the corresponding intensity graph. The layer number is indicated in both figures.

$GeSb_2Te_4$

The second type of block that is formed after annealing a GeTe-Sb_2Te_3 superlattice is the 7-layered variant, $GeSb_2Te_4$. From the experimental data of ref. [6] it is seen that the structure is not symmetric. The sixth layer shows much higher intensities than the second layer. Therefore the composition of $GeSb_2Te_4$ has to be noted with three numbers, corresponding to the occupancy of Sb in layers 2, 4 and 6 respectively. The experimental results are compared to simulations in dr. Probe in the same was as for the 9-layered block. On first guess, the 60-40-100 composition is simulated and based on that result new samples are created. The results are shown in figures 4 and 10 (appendix). The 65-30-90 composition gives a fairly good fit to the experimental data, where the peaks differ only $\pm 1\%$ in intensity. The simulated intensity peaks are somewhat thinner than in the experiments, which could be due to a wrong set probe size. In dr. Probe, a parameter that is related to the probe size (HWHM) is set so it knows how to convolute the images. If this parameter was set too low, the convolution changes and therefore the intensity peaks will be smaller. In this case it is not likely that the probe size parameter is set up wrong, because the same probe was used for both the $GeSb_2Te_4$ and $Ge_2Sb_2Te_5$ images. The latter simulations did match the convolution of the experiments, where the experimental probe size was of course also the same in both cases. It is odd that the $GeSb_2Te_4$ block is asymmetric in occupancies. It was expected that the block would be symmetric because of the annealing process, just as in the case of $Ge_2Sb_2Te_5$. An possible reason could be that the growth direction in the film is still influencing the layers, even after the annealing process. But then one would expect that the $Ge_2Sb_2Te_5$ structure is also still asymmetric, which is not the case. Another explanation could be an experimental error or local fluctuations in the experimental image. This would mean that the image is not representative for $GeSb_2Te_4$ in general. The intensity differences by changing the occupancies of layers 2, 4 and 6 show more Z-dependence than the 9-layered structure. Generally, the layers with highest atomic number show highest intensity peaks.

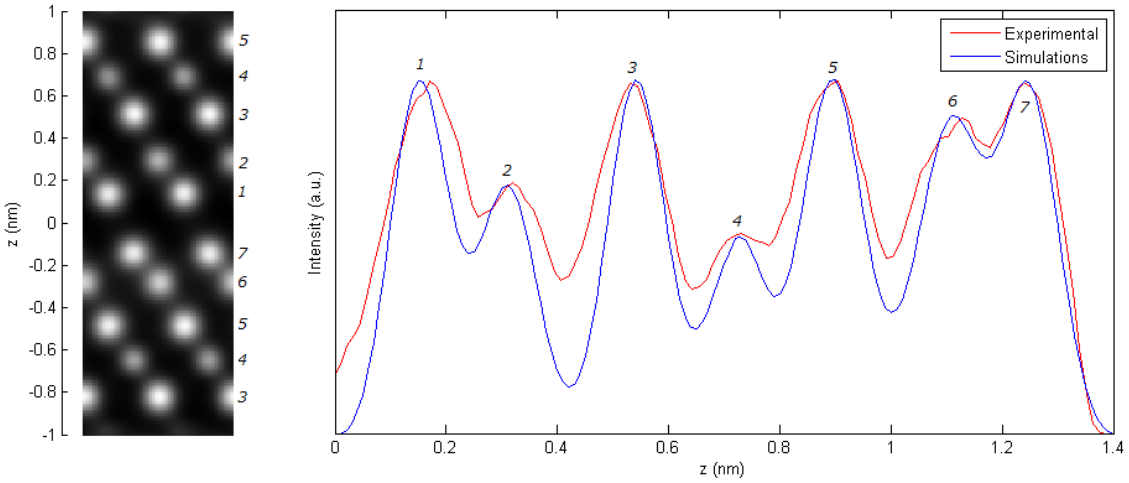

Figure 4: Results of simulating $GeSb_2Te_4$ in dr. Probe with 65-30-90 composition. On the left the convoluted image exported by the software and on the right the corresponding intensity graph. The layer number is indicated in both figures.

Vacancies

In the previous two sections it is assumed for simplicity that all the layers in the GeSbTe blocks are fully occupied. However, other research [11, 20] showed that the Ge/Sb layers in the blocks are often not completely filled. The layers have vacancies, which would suggest the above proposed structures of $Ge_2Sb_2Te_5$ and $GeSb_2Te_4$ are not correct, because the occupancies would add up to 100%. It is likely that the vacancies in the crystal structure influence the STEM-images, because the intensity is proportional to the atomic number. Vacancies in the structure can be seen as a lower (average) atomic number, resulting in lower intensities. To investigate the effect of vacancies, a sample of $Ge_2Sb_2Te_5$ is simulated in dr. Probe with vacancies in only one layer. The total occupancy in layer 2 is lowered without adjusting the other layers. In this way, also the influence

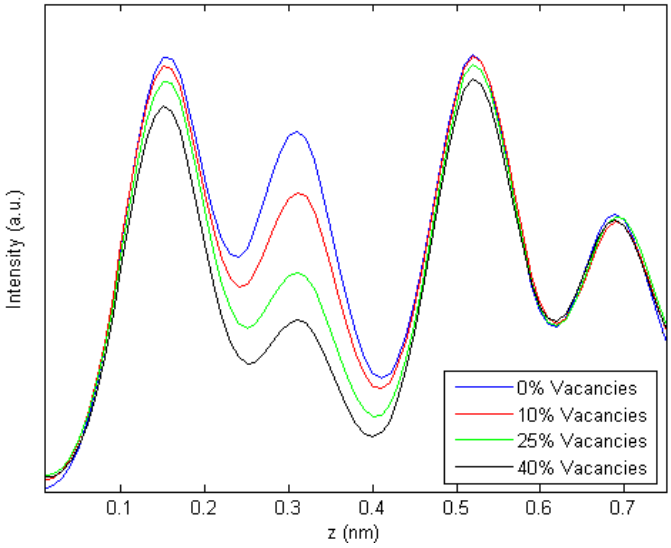

Figure 5: Intensity graphs of the first four layers of $Ge_2Sb_2Te_5$ with different amount of vacancies in the second layer.

on nearby layers can be observed. The ratio between the occupancies of Ge and Sb in the second layer, in this case 1:2, stays constant. The resulting intensity graphs are shown in figure 5. To better look at the changes in the nearby Te peaks, these graphs are not normalized. As expected, the intensity of the second peak decreases as a function of the number of vacancies. Also it can be seen that the intensities of the nearby Te peaks are decreasing. This means that the intensities of the separate layers are definitely influenced by atoms close to it. The deviation in intensity is strongly dependent on the distance from the vacancies. But on small distances (< 0.2 nm) this effect cannot be neglected. Vacancies result in different peak heights of Te and this result also shows that the intensity peaks of Te are influenced by nearby atomic layers. This really questions the way of normalizing in ref. [6], where all Te layers are assumed to have the same intensity.

Frozen lattice approximation

As mentioned before, the simulations in dr. Probe are based on the frozen lattice approximation. To test the consequences of this approach, the same sample is simulated ten times with the same settings. The software will apply the frozen lattice approximation ten times and this leads to ten different images. The intensities along the image show fluctuations, of which the minimum and maximum are shown in figure 6. The difference in minimum and maximum are in the range of 2 to 6 percent of the total intensity. This could be an explanation for the sometimes odd intensity

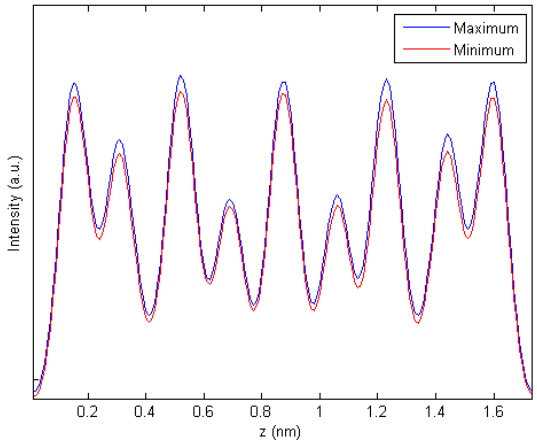

Figure 6: Minimum and maximum intensities of ten different simulations with the same sample and settings.

profiles in figure 9, where the heaviest layers sometimes do not give highest intensities. An error margin of ±3% in the intensity corresponds to an error margin of ±6% in the atomic number of the atoms in the layer. The error margin can of course be reduced if the amount of FL-variants is increased, because the statistical error is proportional to the square root of the number of images averaged over. An error margin of ±6% in the atomic number leads to an error margin of ±3-6% in the partial occupancies proposed in the previous section. The best fitting composition of annealed $Ge_2Sb_2Te_5$ is therefore 65±4% Sb with 35±4% Ge in outer layers 2 and 8 and 35±4% Sb with 65±4% Ge in inner layers 4 and 6. The annealed $GeSb_2Te_4$ blocks therefore consists of 65±4% Sb with 35±4% Ge in layer 2, 30±5% Sb with 70±5% Ge in layer 4 and 90±6% Sb with 10±6% Ge in layer 6.

Other simulation software

In the research of Lotnyk et al. [21] the experimental intensity profiles of HAADF-STEM images are also compared to simulations. In this research, the simulations are based on the absorptive potential approach in the Fast Fourier Transform (FFT) multislice formalism [21,22]. Here, multiple structural models are used to see which fits best to the experimental data. By using the same structural parameters and microscope settings, one of these structures (pure $Ge_2Sb_2Te_5$) is also simulated in dr. Probe to see the differences between both software. The results are shown in figure 7, with on the left the simulation by Lotnyk et al. and on the right the intensity peaks of a simulation using dr. Probe. The Te and Sb peaks have more or less the same intensity in both cases, were on the left the Sb peaks are slightly lower. The Ge peaks do not match in both cases according to the y scale, but both software packages normalize the intensity profiles in a different way. It is expected that the intensity of a vdW gap on the left is also higher than on the right. If both techniques would use the intensities from vdW gaps to the maximum (interesting part) for the normalization, the intensity peaks are maybe much closer. From these two figures, it is hard to make statements about the quality and suitability of dr. Probe.

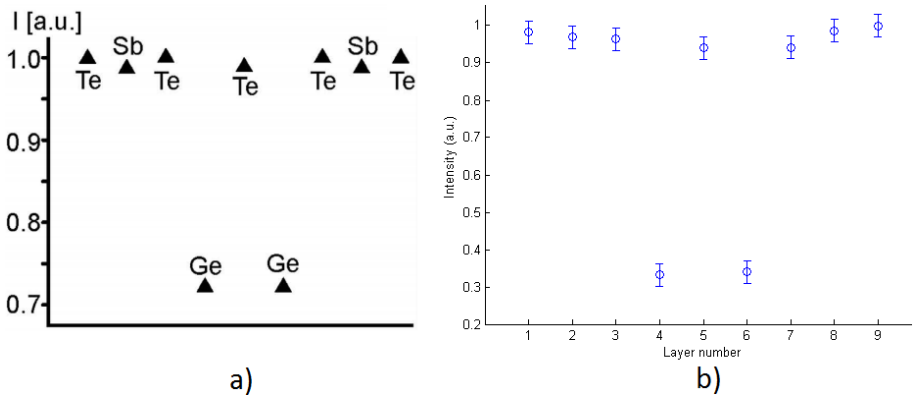

Figure 7: Comparison of simulating techniques of HAADF-STEM images. With a) the absorptive potential approach in the FFT multislice formalism from ref. [21] and b) the own results with dr. Probe.

Discussion

It was possible to give information about the structure and the occupancies of the atomic layers, but some remarks have to be made. The frozen lattice approximation used in the simulation software leads to error margins for every intensity graph. Therefore, it is not possible to determine occupancies of certain atomic layers with a very high accuracy. This error margin corresponds to fluctuations of maximal ±6% in the average atomic number of the layers. This margin could be decreased by using more variants per slice for the FL approximation. To use more FL-variants a computer with more memory is required, because the amount of FL-variants scales linearly with the required memory. Secondly, the simulations showed that the way of normalizing of ref. [6] is highly debatable. The normalization is based on the assumption that the same atomic layers show same intensity. This normalization is done to rule out some intensity fluctuations in the

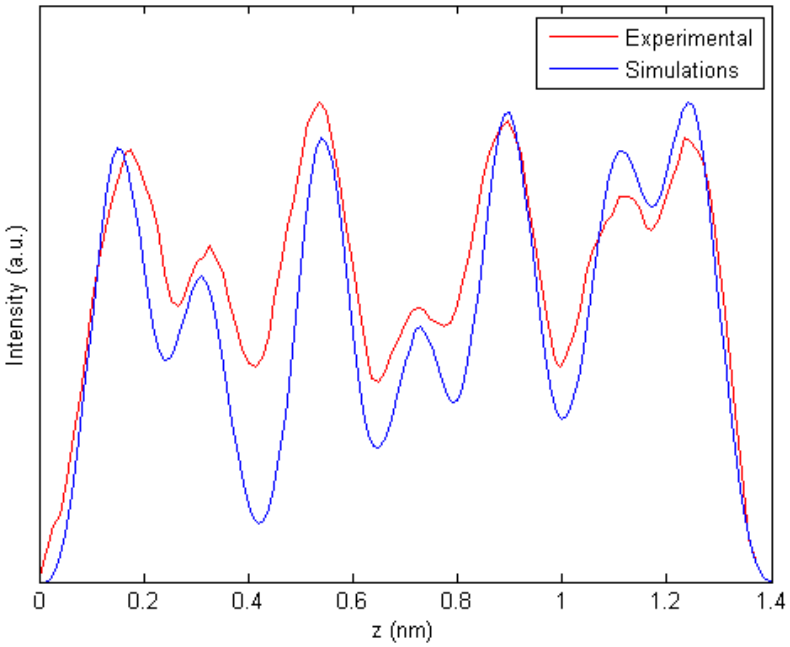

Figure 8: Unnormalized intensity graphs for $GeSb_2Te_4$ of experiments and simulations using 65-30-90 composition.

experimental images, for example stains, thickness variations and contamination. As seen from figure 5, the intensity of some layer is not only dependent on the atoms in its own layer, but also on nearby atoms. This can result in Te peaks that do not have the same intensity. In this way the polynomial used for the normalization changes the Ge/Sb peaks in a wrong way. Also, when comparing the unnormalized intensity data in figure 8, it is seen that the 65-30-90 composition does not fit the experimental images as well as initially thought. Based on the simulations it is therefore recommended to normalize the images in a different way. For example, the images could be normalized by using only one (e.g. the first) Te peak of every $GeSb_2Te_4$ or $Ge_2Sb_2Te_5$ block. In this way, only the peaks that should be identical are properly taken into account, instead of local fluctuations by nearby atoms. This is only possible if multiple blocks of the same type are next to each other, which is not always the case. The images of ref. [6] show large fluctuations in intensities, making it hard to say something quantitative about the individual layers. This is due to the small width of the images and the small amount of blocks encountered. The STEM images could be compared to the simulations more accurately if the experimental intensity profiles are averaged over larger regions. If the STEM used in the experiments is of a better quality (e.g. higher accelerating voltage) the experimental images could also be better compared to the simulations. At last, dr. Probe is also compared to other simulating techniques. The different images show the same shape, but with deviating scale. Therefore no conclusions on the usability of dr. Probe can be drawn from this comparison. If more time and computing power is available, these and other software packages can be compared more extensively to see which is best suitable for simulating HAADF-STEM images.

Conclusions

The present work has shown that computer simulation of HAADF-STEM images by dr. Probe is a useful tool for comparing and understanding experimental HAADF-STEM images. The combination with VESTA turns out to be very suited in this respect. According to theoretical simulations of HAADF-STEM imaging, the composition of the annealed $Ge_2Sb_2Te_5$ blocks in ref. [6] is 65±4% Sb with 35±4% Ge in outer layers 2 and 8 and 35±4% Sb with 65±4% Ge in inner layers 4 and 6. The annealed $GeSb_2Te_4$ blocks consists of 65±4% Sb with 35±4% Ge in layer 2, 30±5% Sb with 70±5% Ge in layer 4 and 90±6% Sb with 10±6% Ge in layer 6. The partial occupancies are based on comparing the simulated images with the normalized images of ref. [6], where the simulations showed that this way of normalizing may be incorrect. It cannot be assumed that

all atomic layers of Te always have the same intensity, because the intensity is also influenced by nearby atomic layers. Simulations with exactly the same sample and settings can give slightly different images due to the frozen lattice approximation. This results in error margins of ±6% in determining the average atomic number of the Ge/Sb layers. This error can be decreased by using more FL-variants. Comparing the raw unnormalized images showed that the quality of the HAADF-STEM images of ref. [6] should be improved in order to make really accurate statements about the occupancies of the atomic layers. If the quality of the experimental images could be improved and more computing power is available, the simulations by dr. Probe are a valuable method to compare experimental data to computer simulations. In this way, partial occupancies of the atomic layers in different GeTe-Sb_2Te_3 superlattices could be determined with high accuracy.

Appendix: Supplementary figures

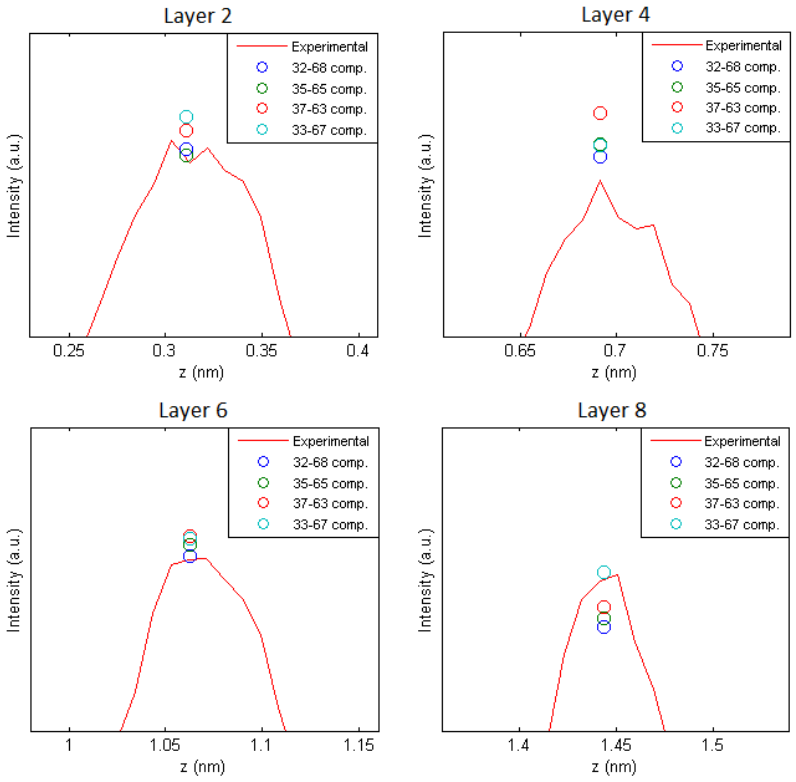

Figure 9: Partial intensity graphs of simulations with different compositions of $Ge_2Sb_2Te_5$.

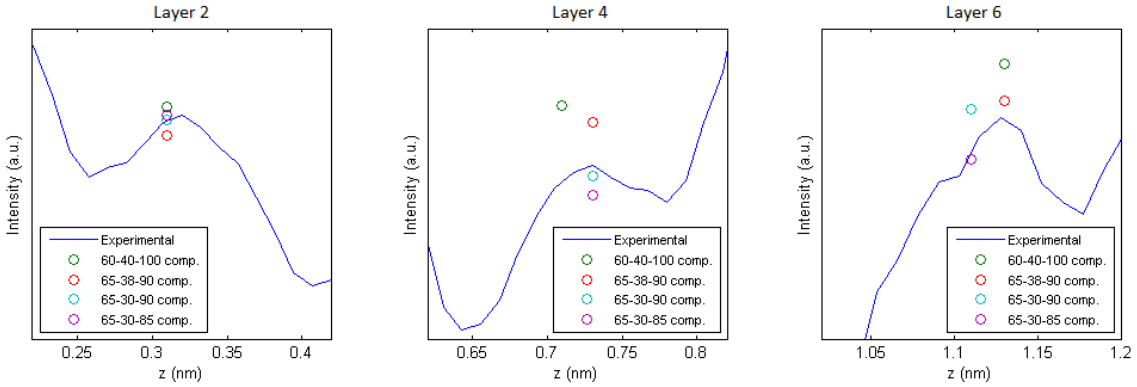

Figure 10: Partial intensity graphs of simulations with different compositions of $GeSb_2Te_4$.

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