The electrodeposition of germanium antimony telluride (GST) alloys from a single non-aqueous plating bath based on tetrabutylammonium chlorometallate precursors is presented. The system provides a case-study for plating bath optimization in order to produce complex functional materials. GST deposits in the amorphous phase and the film composition and morphology can be readily adjusted by tuning the three precursor concentrations and the electrodeposition potential. Adjustment of the precursor concentrations allows the preparation of deposits ranging from the binaries (GeSb, GeTe, Sb$_2$Te$_3$) to ternaries with a wide range of compositions, including the standard GeSb$_2$Te$_5$ composition – more commonly known as GST-225 – which is widely used in the solid state memory industry. In this paper we present a detailed study discussing the complex interplay between the deposition of germanium, antimony and tellurium and how adjusting the concentrations of their chlorometallates allows control over the composition and also the morphology of the deposits. We also highlight the benefits that arise from the wide separation in the deposition potentials for the three precursors, and in particular the ability to control the composition through modulation of the deposition potential.

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areas were prepared using sputtering techniques. The masking layer porting electrolyte. confirmed by comparison to a standard Ge2Sb2Te5 sample prepared by Rigaku SmartLab diffractometer (Cu-Kα). Change materials in the electronics industry. The initial voltammetry of the electrodes was chosen for all experiments. 2.0 to 1.0 V. A starting potential of 0.3 V (slightly anodic of the open circuit potential) was chosen for all experiments. Voltammetric characterization was performed using glassy carbon working electrodes, a Pt mesh counter electrode and a home-made Ag/AgCl (0.1 mol dm−3 [NaCl] in CH2Cl2) reference electrode in an undivided electrochemical cell. The glassy carbon electrodes were made in-house from 3 mm diameter glassy carbon rod (Sigradur G, HTW) heat sealed into glass tubes. Prior to the experiments the glassy carbon electrodes were polished in a four-stage process to ensure a fresh surface: The electrodes were first resurfaced on wet lapping film (SMIC grade, Al2O3, 3M). The electrodes were then sequentially polished with wet 1 μm, 0.3 μm and 0.05 μm alumina powders (MicroPolish or MicroPolishIII, Buehler) on a nap cloth (Microcloth, Buehler). Ultrapure water (18.2 MΩ cm, Pur1te) was used throughout as the lubricant and for rinsing. The electrodes were finally dried under an argon stream before transferring into the glove box. The Pt mesh counter electrode was cleaned by rinsing under ultrapure water and heating in a butane/propane mix flame (70% butane, 30% propane, Campingaz). The reference electrode was stored in 0.1 mol dm−3 [NaCl] in CH2Cl2 inside the glove box. Cyclic voltammograms were recorded at a scan rate of 50 mV s−1 in a potential window from −2.0 to 1.0 V. A starting potential of 0.3 V (slightly anodic of the open circuit potential) was chosen for all experiments. TiN substrates were used for the electrodeposition of GST alloys, since they represent the most common substrate used for phase change materials in the electronics industry. The initial voltammetric characterization was performed on glassy carbon due to the higher resistivity of the TiN films (see supporting information). TiN substrates consisting of a 2 × 1 cm2 silicon chip with a 500 nm SiO2 backing layer, a 200 nm TiN conducting layer and a 200 nm SiO2 masking layer defining the electrode (0.126 cm²) and contact areas were prepared using sputtering techniques. The masking layer was patterned using a lift-off process. The electrodeposition procedure consisted of an initial 5 s 0.5 V equilibration step followed by a single potentiostatic electrodeposition step. The length of the electrodeposition step was either defined by a set cutoff charge relating to a chosen nominal deposit thickness or by the deposition time. The deposition potential was varied to study its effect on the deposits. It must be noted that determining the film thickness using the charge is only approximate since the faradaic efficiency of the electrodeposition process is not known exactly.

Characterization.—A Philips XL30 ESEM scanning electron microscope (SEM) was used to image the deposits. An acceleration voltage of 10 kV and a working distance of approximately 10 mm were used for all measurements. The elemental composition was determined by energy dispersive X-ray spectroscopy (EDX) using a Thermo Scientific NORAN System 7 X-ray Microanalysis System. The composition was determined in spectrum mode on an approximately 2800 μm² area. The calibration of the instrument was confirmed by comparison to a standard Ge2Sb2Te5 sample prepared by PVDF. X-ray diffraction of the annealed deposits was performed on a Rigaku SmartLab diffractometer (Cu-Kα) with a 1° grazing incidence angle and a Detex250 1D detector. Data were fitted using the GSAS package in Le Bail mode, with structure models from ICSD. All samples were annealed in a Jipelec Rapid Thermal Annealer system.

Results and Discussion

The effects of a range of factors on the obtained deposits are discussed in this article. The results and discussion are structured into the following sections: i) voltammetric characterization of the precursor species and ii) the alloy plating baths; composition of as-deposited thin films as a function of iii) the plating bath composition, iv) the plating bath concentration, v) the deposition potential and vi) crystallographic characterization of annealed deposits as a function of the thin film composition.

Sample labeling.—In this paper individual deposits are labeled using bold capital Latin letters and relevant additional information to provide an overview over the 61 different deposits discussed. A summary of all the samples including information about the deposition potential (Em), the nominal deposit thickness (d) and the plating bath composition are provided in the Supplementary Information in Table S1.

Voltammetric characterization of the precursor species.—In order to understand the alloy plating baths, it is essential to characterize the voltammetry of the individual precursors. Figure 1 presents cyclic voltammograms recorded in plating baths containing the germanium (a), antimony (b) or tellurium (c) chlorometallates, respectively.

Several papers exist describing Ge deposition from non-aqueous plating baths. In these plating baths hydrogen evolution, which generally competes with Ge deposition in aqueous systems, can be avoided. Ge has been deposited from deep eutectics, organic and supercritical solvents. In our research we use a non-aqueous plating bath to facilitate the incorporation of Ge into the material.

The germanium voltammogram (Figure 1a) is characterized by two major cathodic peaks at −0.7 V (c2) and −1.6 V (c3) which can be associated with the reduction of GeIV → GeII and the reduction of GeII → Ge0, respectively. On the reverse scan two plateaus are observed, suggesting diffusion controlled regions for both reduction reactions. A nucleation loop is not observed for this species. The voltammetry is irreversible and no stripping peak was observed in the investigated potential range. During the cyclic voltammetry a layer of germanium was deposited on the electrode surface.

After the first cycle the current densities of the reduction peaks are reduced. Since germanium is a semiconductor with a significant bandgap of 0.66 eV it is conceivable that the deposit introduces a non-conducting layer on the electrode surface, hindering the electrochemical processes. When electrodeposition germanium at a constant potential the current generally falls to zero over time. This suggests that the maximum deposit thickness is self-limiting; probably related to the conductivity of the deposited germanium layer. A small preceding peak at −0.2 V (c1) was also observed in the first scan. Similar preceding peaks were observed by Endres and co-workers when studying the electrodeposition of germanium from GeCl4 in an ionic liquid using gold electrodes and by our group studying the electrochemistry of [GeCl4][F] complexes in CH2Cl2 using a Pt disc working electrode. Since c1 is only present in the first scan, but occurs on a range of different substrates, including glassy carbon, Pt and Au it may be related to non-specific interactions between GeIV ions and the electrode surface.

The voltammetry of the antimony (Figure 1b) and tellurium precursors (Figure 1c) were discussed previously.

The voltammetry of [NBu4][SbCl4] is characterized by a reduction peak at −0.83 V (c1), followed by the onset of a second peak at approximately −1.8 V (c2) and a stripping peak (a1) at 0.73 V (Figure 1b). A nucleation loop associated with the deposition of antimony is clearly visible. The deposition onset potential for antimony is at −0.4 V on glassy carbon and the nucleation overpotential is −0.23 V. The first reduction peak (c1) can be attributed to the reduction of Sb4+ to Sb3+. As confirmed by the ability to electrodeposit antimony
Cyclic voltammetry of $1 \times 10^{-2}$ mol dm$^{-3}$ [NBu$_4$]$_2$[GeCl$_5$] (a), [NBu$_4$]$_2$[SbCl$_4$] (b) and [NBu$_4$]$_2$[TeCl$_6$] (c) in 0.1 mol dm$^{-3}$ [NBu$_4$]$_2$Cl in CH$_2$Cl$_2$ measured at a scan rate of 50 mV s$^{-1}$. The solid light gray line shows the voltammetry of the pure supporting electrolyte (SE). Arrows indicate the starting potential (0.3 V) and the scan direction. Glassy carbon, platinum gauze and Ag/AgCl (0.1 mol dm$^{-3}$ [NBu$_4$]$_2$Cl in CH$_2$Cl$_2$) were used as working, counter and reference electrode, respectively.

The reverse current in the potential region of c$_2$ is diffusion limited at these potentials using this system. The origin of the second reduction peak (c$_2$) is unclear. When cycling an as-deposited Sb film in the pure supporting electrolyte (0.1 $\times$ 10$^{-3}$ mol dm$^{-3}$ [NBu$_4$]$_2$Cl in CH$_2$Cl$_2$) both reduction peaks are visible in the first scan but disappear in subsequent scans, probably due to removal of trapped reagents in the deposits. No significant changes are visible when inspecting the deposits visually before and after cycling in the supporting electrolyte excluding deposit stripping as a cause for the peak disappearance. It is thus assumed that c$_2$ is indeed related to the antimony precursor species.

The reverse current in the potential region of c$_2$ is diffusion limited and indistinguishable from the reverse current in the potential region of c$_1$, suggesting that the same electrochemical process occurs across the whole potential range. Previous works on the voltammetry of antimony species in ionic liquids, molten salts and our own CH$_2$Cl$_2$ work have not shown the second peak, as it is outside the potential range investigated in those studies. In this paper we employed a wider potential range since the deposition of GST is performed in that region. It must be noted that the electrodeposition of Sb (at least as part of a compound) is possible from potentials more cathodic than $-1.5$ V. A main stripping peak (a$_1$) at 0.7 V and a small preceding shoulder at around 0.35 V are observed. The preceding peak can be attributed to c$_2$, as it is not present when the scan direction is reversed before c$_2$. The total stripping charge is approximately 3.6 times smaller than the deposition charge. The lower stripping charge may be due to the low adherence of Sb to the electrode surface. Upon continued scanning, the magnitude of the stripping peak decreases. The reduction peaks remain relatively constant.

The onset of the tellurium reduction was at approximately $-0.05$ V (Figure 1c). However, the first reduction peak (c$_1$) is only established at $-1.25$ V. A nucleation loop with a nucleation overpotential of approximately $-0.35$ V was observed for [NBu$_4$]$_2$[TeCl$_6$]. The deposition of tellurium onto glassy carbon requires a significantly higher over-potential. Subsequent further tellurium deposition is easier, as can be seen by the earlier onset of the reduction current. The second and third scans also exhibit much larger currents at the more anodic potentials and show a further reduction peak (c$_2$) at $-1.7$ V. These peaks are likely related to the further reduction of Te$^0$ to Te$^{VI}$, evident in the reverse scan direction by two distinct diffusion controlled regions. The voltammetric behavior of [NBu$_4$]$_2$[TeCl$_6$] is very complex due to the formation of Te$^{VI}$. A small stripping peak (a$_1$), suggesting poor dissolution of the Te deposit, was observed at 0.77 V. Other groups have discussed the electrochemical properties of Te$^{IV}$ species, but the electrochemical behavior of tellurium is very sensitive to the plating bath and the observed voltammograms differ widely.

**Voltammetric characterization of the alloy plating bath.** It is possible to combine the Ge$^{IV}$, Sb$^{III}$ and Te$^{IV}$ chlorometallate compounds into a single chemically stable plating bath and deposit functional alloy materials. This allows a fine control over the composition of the deposits the complex electrochemical behavior of the plating bath must be investigated. By screening a range of precursor ratios, the features observed in the voltammograms of the resulting plating baths were assigned to the three elements.

Figure 2 illustrates the changes observed when incrementally increasing the concentration of one precursor species in the plating bath. By comparison to Figure 1 it is apparent that the observed peak potentials are shifted compared to the peak potentials identified for the individual precursors indicating interactions between the precursor species during electrochemical deposition.

In Figure 2 three sets of voltammograms are contrasted. Each column represents data recorded in plating baths containing constant concentrations of two elements (e.g. $1 \times 10^{-3}$ mol dm$^{-3}$ [NBu$_4$]$_2$[SbCl$_4$] and $2 \times 10^{-3}$ mol dm$^{-3}$ [NBu$_4$]$_2$[TeCl$_6$] for Figures 2a–2f) and an increasing concentration of the third element starting from $0 \times 10^{-3}$ mol dm$^{-3}$ in the top row to approximately double the previously determined standard concentration in the bottom panel. The standard pre-cursor bath concentration required for the deposition of Ge$_2$Sb$_2$Te$_5$ is (1 : 1 : 2) $\times 10^{-3}$ mol dm$^{-3}$ [NBu$_4$]$_2$[GeCl$_5$] : [NBu$_4$]$_2$[SbCl$_4$] : [NBu$_4$]$_2$[TeCl$_6$] and three independent examples of representative voltammograms are shown in Figures 2d, 2j and 2p with the gray background. Comparison of these three data sets shows that there is excellent reproducibility in these experiments.

Each element causes some obvious changes to the voltammetry, in addition to some more subtle effects. Germanium addition (Figures 2a–2f) causes a significant suppression of the stripping currents and quenches the current density measured in the reverse scans; especially for the second and third scans the current density can drop to nearly zero. Germanium addition also appears to cause the most cathodic peak (c$_4$), which is not observed in the voltammogram for Sb Te only (Figure 2a). In addition, the presence of germanium in the plating bath also leads to the formation of the c$_1$ peak, which is the germanium pre-peak discussed previously (see c$_1$ peak in Figure 1a).

Antimony addition significantly increases the current density of the first and third cathodic peaks (c$_2$ and c$_4$) (Figures 2g–2i) while c$_3$ remains unchanged. A slight increase in the stripping current was observed for high concentrations of antimony.

Figure 1. Cyclic voltammetry of $1 \times 10^{-2}$ mol dm$^{-3}$ [NBu$_4$]$_2$[GeCl$_5$] (a), [NBu$_4$]$_2$[SbCl$_4$] (b) and [NBu$_4$]$_2$[TeCl$_6$] (c) in 0.1 mol dm$^{-3}$ [NBu$_4$]$_2$Cl in CH$_2$Cl$_2$ measured at a scan rate of 50 mV s$^{-1}$. The solid light gray line shows the voltammetry of the pure supporting electrolyte (SE). Arrows indicate the starting potential (0.3 V) and the scan direction. Glassy carbon, platinum gauze and Ag/AgCl (0.1 mol dm$^{-3}$ [NBu$_4$]$_2$Cl in CH$_2$Cl$_2$) were used as working, counter and reference electrode, respectively.

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Figure 2. Cyclic voltammograms recorded in plating baths containing varying concentrations of $[\text{NBu}_4]_2[\text{GeCl}_5]$ (a–f), $[\text{NBu}_4]_2[\text{SbCl}_4]$ (g–l) or $[\text{NBu}_4]_2[\text{TeCl}_6]$ (m–r). The gray panels (d, j, p) represent voltammograms obtained on identical plating baths and highlight the reproducibility of the system. Three consecutive scans recorded at 50 mV s$^{-1}$ are shown and the voltammetric response of the pure supporting electrolyte is included (SE, light gray curve). The arrows in (j) indicate the scan origin and the scan direction valid for all scans. The precursor ratios are quoted in the panels ($c([\text{NBu}_4]_2[\text{GeCl}_5]) : c([\text{NBu}_4]_2[\text{SbCl}_4]) : c([\text{NBu}_4]_2[\text{TeCl}_6]$ in 10$^{-3}$ mol dm$^{-3}$) and only one precursor concentration is adjusted per column. The plating baths were prepared in CH$_2$Cl$_2$ with 0.1 mol dm$^{-3}$ $[\text{NBu}_4]\text{Cl}$ as the supporting electrolyte. A 3 mm diameter glassy carbon, a $\sim$1 cm$^2$ platinum gauze and an Ag/AgCl (in 0.1 mol dm$^{-3}$ $[\text{NBu}_4]\text{Cl}$ in CH$_2$Cl$_2$) working, counter and reference electrode were used.
Tellurium addition (Figures 2m–2r) shifts the reduction onset potential by +0.17 V, indicating that tellurium significantly facilitates the material deposition onto glassy carbon. Similar to the addition of germanium, an increasing tellurium concentration leads to an increase in the c3 peak.

As the behavior of peak c3 demonstrates, the increase in the various peak currents with increasing precursor concentrations is complex and the peak intensities are dependent on more than one plating bath species. This is partly caused by changes in the background due to the peak overlaps. However, the effects are too clear to be explained by background currents alone. Plots of the peak currents as a function of the incrementally-added plating bath species can be found in the supporting information (Figure S1).

While peak c3 remains relatively stable when incrementally adding one of the precursor species to the plating bath (changes in the peak positions are illustrated in Figure S2). The one major exception to this is a significant anodic shift in c2 (by +0.17 V) and c3 (by +0.27 V) upon adding the first increment of tellurium (compare Figures 2m and 2n). Peak c2 remains relatively constant after the first addition and the current density remains quite constant. Peak c3 shifts back toward the initial potential as the current density increases once more tellurium was added to the plating bath. Other peak shifts were also observed, such as a cathodic shift in c4 when adding more antimony to the plating bath. However, the peak is not very clear and precise determination of the peak position was not possible.

**Thin film properties as a function of the plating bath composition.**—GST films were prepared on TiN substrates from the plating bath. However, the peak is not very clear and precise determination of the peak position was not possible.

Deposits were characterized by SEM and EDX analyses to understand the effect of the three precursors on the composition and the morphology. Figure 3 shows SEM images of the thin deposits obtained from a plating bath with 0 mM \([NBu_4][GeCl_5]\) to deposits with a 39% : 13% : 48% Ge : Sb : Te composition for 2.5 × 10⁻³ mol dm⁻³ \([NBu_4][GeCl_3]\), \([NBu_4][SbCl_5]\) and \([NBu_4][TeCl_6]\) were present in 1 × 10⁻³ mol dm⁻³ and 2 × 10⁻³ mol dm⁻³ concentrations in the plating bath. If the two elements were plated at similar rates this should have led to a SbTe₂ composition. The lack of deposited antimony in the pure Sb-Te plating bath highlights that the electrodeposition of GeSbTe compounds is not straightforward. In addition, it appears that the added germanium substitutes antimony in the deposit: initially the tellurium content decreased rapidly when more \([NBu_4][GeCl_3]\) was added to the plating bath. However, for germanium precursor concentrations of more than 1 × 10⁻³ mol dm⁻³ the tellurium content remained relatively constant at around 45%, while the antimony content in the deposits decreased significantly from a maximum of approximately 20% to nearly zero. A 1 × 10⁻³ mol dm⁻³ \([NBu_4][GeCl_3]\) concentration leads to a deposit composition of approximately Ge₅Sb₂Te₇. This is the preferred composition for solid state memory alloys and it appears that the alloy also favors approximately 20% vacancies in the Ge : Sb sublattice. This may explain why the added germanium mostly replaces the antimony in the deposit, as the two elements compete for the same sites in the deposits.

An increased Sb concentration in the plating bath (Figures 4b, 4c) causes a relatively linear addition of antimony into the deposits. This is particularly apparent in the data representation provided in (e). The original GeTe deposits were very tellurium rich, with tellurium contents of above 80%. Interestingly, the addition of antimony appears to displace the tellurium, while the germanium concentration remains more constant. The composition shows a linear behavior when represented in a composition triangle (Figure 4b). When extrapolating the data to the GeSb line a composition of approximately Ge₃Sb₄ would be expected.

In general, it appears that tellurium is the most dominant of the plating bath species. Increase in the tellurium precursor species leads to a relatively linear increase of tellurium in the deposits and the antimony to germanium ratio remains relatively stable. When adding germanium to the deposits the composition tends toward a GeSb₂Te₅. This is particularly apparent in the data representation provided in (e). The original GeTe deposits were very tellurium rich, with tellurium contents of above 80%. Interestingly, the addition of antimony appears to displace the tellurium, while the germanium concentration remains more constant. The composition shows a linear behavior when represented in a composition triangle (Figure 4b). When extrapolating the data to the GeSb line a composition of approximately Ge₃Sb₄ would be expected.
Figure 3. Scanning electron micrographs (2000 × magnification) of electrodeposited GST thin films (nominal thickness was 200 nm) as a function of the precursor concentration in the plating bath. Bold capital letters refer to the sample IDs. Two precursors were kept at constant concentrations while the third precursor concentration was varied. The concentrations (c/10⁻³ mol dm⁻³) of the three precursors are provided in the figure in the order \([\text{NBun}_4][\text{GeCl}_5] : 3 [\text{NBun}_4][\text{SbCl}_4] : 3 [\text{NBun}_4][\text{TeCl}_6]\). 0.1 mol dm⁻³ [NBun₄]Cl was used as the supporting electrolyte. All films were deposited on TiN substrates (4 mm diameter exposed area, masked with SiO₂) at a potential of −1.75 V vs. Ag/AgCl (0.1 mol dm⁻³ [NBun₄]Cl in CH₂Cl₂). A Pt gauze was used as the counter electrode. SEM images of thicker GST deposits appear quite similar and are provided in the supporting information (See Figure S3). The scale bars represent 10 μm.

rates. GST deposits were thus also prepared from plating baths with higher net chlorometallate concentrations. The concentration ratio of the precursors was fixed to \([\text{NBun}_4][\text{GeCl}_5] : [\text{NBun}_4][\text{SbCl}_4] : [\text{NBun}_4][\text{TeCl}_6] = 1 : 1 : 0.6\) and was sequentially increased by a factor of 10. The concentration of the supporting electrolyte was kept constant at 0.1 mol dm⁻³.

Figure 5 summarizes the voltammetry, the deposit morphology and the composition as a function of the net plating bath concentra-
tion. As expected, the morphology of the deposits becomes grainier when the plating bath concentration was increased, due to the faster deposit formation rate. The most concentrated plating baths produced deposits with a homogeneous surface appearance consisting of large globular features covering the whole electrode. These features were smaller for the deposits obtained from less concentrated plating baths and the irregular overlayer discussed previously is developed (cf. Figure 3). Rather less expected was that the rate of tellurium deposition
Figure 4. Change in the composition of electrodeposited GST thin films as a function of the precursor concentration in the plating bath represented as composition triangles (a – c) and scatter plots (d – f). Two precursors were kept at constant concentrations of $1 \times 10^{-3}$ mol dm$^{-3}$ for [NBun$_4$][GeCl$_5$] and [NBun$_4$][SbCl$_4$] or $2 \times 10^{-3}$ mol dm$^{-3}$ for [NBun$_4$$_2$][TeCl$_6$] while the third precursor concentration was varied from 0 to approximately double the standard concentration. The composition was determined by EDX and was obtained while scanning across 2,800 $\mu$m$^2$ areas. The composition shown is an average obtained from at least three different areas evenly spaced across the whole sample. The composition is representative of the average deposit composition. The labels in the triangle plots (a – c) and on the top axis of the scatter plots (d – f) correspond to the sample IDs. The pink star corresponds to the reference GST-225 sample. All films were deposited on TiN substrates (4 mm diameter exposed area) at a potential of $-1.75$ V vs. Ag/AgCl (0.1 mol dm$^{-3}$ [NBun$_4$]Cl in CH$_2$Cl$_2$). A Pt gauze was used as the counter electrode. Table S2 provides the numerical data of the EDX quantification.

Figure 5. Cyclic voltammograms recorded on glassy carbon (a – d) and SEM images (e – h) and EDX quantification (i) of deposits S × 1, S × 2, S × 5 and S × 10. The GeSbTe deposits were obtained on TiN substrates at different net plating bath concentrations ranging from (1 : 1 : 0.6) $\times 10^{-3}$ mol dm$^{-3}$ [NBun$_4$][GeCl$_5$] : [NBun$_4$][SbCl$_4$] : [NBun$_4$$_2$][TeCl$_6$] to (10 : 10 : 6.2) $\times 10^{-3}$ mol dm$^{-3}$ in 0.1 mol dm$^{-3}$ [NBun$_4$]Cl in CH$_2$Cl$_2$. A Pt gauze counter electrode and an Ag/AgCl (0.1 M [NBun$_4$]Cl in CH$_2$Cl$_2$) reference electrode were used throughout. Table S4 provides the numerical data of the EDX quantification.
Figure 6. Composition of deposits obtained from a plating bath containing $10 \times 10^{-3}$ mol dm$^{-3}$ $[\text{NBu}_4][\text{GeCl}_5]$, $10 \times 10^{-3}$ mol dm$^{-3}$ $[\text{NBu}_4][\text{SbCl}_4]$ and $6.2 \times 10^{-3}$ mol dm$^{-3}$ $[\text{NBu}_4][\text{TeCl}_6]$. The composition is represented as a composition triangle (a) and as a 2-axis composition plot (b). Similar plots for other plating bath concentrations are provided in the supplementary information (Figure S5). Table S5 provides the numerical data of the EDX quantification.

Effect of deposition potential on the composition.—Figure 1 highlighted that Ge, Sb and Te have very different deposition potentials, with a potential difference of up to 1 V. This provides another degree of freedom for the tuning of the deposit composition by adjusting the deposition potential. The effect of the deposition potential on the composition of GST was thus investigated. This was done for seven different tellurium concentrations. Figure 6 shows the results for one tellurium concentration and is representative of the general behavior. It shows the effect of the deposition potential on the composition of the deposited material. By changing the deposition potential from $-2$ V to $-1.5$ V the concentration of Ge in the deposits can be significantly reduced and SbTe deposits are obtained. This opens up the possibility to fine-tune the composition of the deposits at a final stage after the plating bath was optimized.

Crystallographic characterization as a function of thin film composition.—The as-deposited GST films are amorphous, as was discussed previously. Considering the non-uniform appearance of the surfaces and the electrochemical deposition behavior, which indicates the formation of a solid solution, deposits from plating baths containing $10 \times 10^{-3}$ mol dm$^{-3}$ $[\text{NBu}_4][\text{GeCl}_5]$, $10 \times 10^{-3}$ mol dm$^{-3}$ $[\text{NBu}_4][\text{SbCl}_4]$ and varying concentrations of $[\text{NBu}_4][\text{TeCl}_6]$ were annealed at 200$^\circ$C for 15 min under a nitrogen atmosphere and investigated by XRD to determine if and what kind of GST and SbTe alloys were formed.

Figure 7 presents XRD data for deposits obtained from plating baths with different tellurium concentrations at $-1.75$ V. The XRD pattern of an annealed GST standard prepared by PVD is also included (PVD standard).
Figure 8. Lattice parameters of the trigonal phases shown in Figure 7 (gray squares) compared with values for various compositions from ICSD (different colored circles). The two plots show lattice parameters with $c \approx 11$ Å (a) and $c \approx 30$ Å (b). ICSD card numbers, compositions and lattice parameters are listed in the supplementary information, Tables S5-S7.

Figure 9. XRD patterns of GST deposits obtained at different deposition potentials in a plating bath containing $10 \times 10^{-3}$ mol dm$^{-3}$ [NBun$_4$][GeCl$_5$], $10 \times 10^{-3}$ mol dm$^{-3}$ [NBun$_4$][SbCl$_4$] and $6.17 \times 10^{-3}$ mol dm$^{-3}$ [NBun$_2$]$_2$[TeCl$_6$]. The XRD pattern of an annealed GST standard prepared by PVD is also included (PVD standard).

Figures 7, 8, S6 and S7, respectively) resulted in lattice parameters close to those of Sb-rich GST phases (Figure 8). Structurally this phase adopts the same stacking sequence as elemental Sb (Table S8), and one Sb pattern in ICSD also had lattice parameters very close to these. U-1.75 V ($\text{Ge}_{0.29}\text{Sb}_{0.38}\text{Te}_{0.33}$) also contained a second phase with a longer c-axis (see Figures 8 and S7) and this became the main Ge-Sb-Te phase as the Te concentration was increased in W-1.75 V ($\text{Ge}_{0.15}\text{Sb}_{0.25}\text{Te}_{0.60}$) (Figures 8, 9 and S8); Y-1.75 V ($\text{Ge}_{0.13}\text{Sb}_{0.24}\text{Te}_{0.63}$) (Figures 8 and S9) and X-1.75 V ($\text{Ge}_{0.08}\text{Sb}_{0.14}\text{Te}_{0.78}$) (Figures 8 and S10). Peaks due to Te also became increasingly prominent and are dominant in the most Te-rich composition. The lattice parameters for the Ge-Sb-Te phase varied smoothly as expected for the varying composition, but comparison with literature phases (Figure 8) shows that Sb-Te phases along with some GST compositions are the main comparisons available for this structure type. Unfortunately there is a large range of reported values for Sb$_2$Te$_3$ and it is not possible to infer the composition accurately by comparing the lattice parameters with literature compositions. However, it is clear that the composition of the crystalline components after annealing is changing and that in most cases more than one crystalline phase is present. Refined patterns are available in the supplementary information (Figures S6-S12). Significant amounts of SbTe were also observed in a PVD prepared GST sample annealed under the same conditions (Figure 7, PVD standard), suggesting that the GST prepared by electrodeposition is comparable to conventionally prepared GST.

In Figure 9 XRD data for deposits W-1.5 V, W-1.75 V and W-2 V – obtained from a plating bath containing $10 \times 10^{-3}$ mol dm$^{-3}$ [NBun$_4$][GeCl$_5$], $10 \times 10^{-3}$ mol dm$^{-3}$ [NBun$_4$][SbCl$_4$] and $6.17 \times 10^{-3}$ mol dm$^{-3}$ [NBun$_2$]$_2$[TeCl$_6$] at different deposition potentials – are shown. The compositions of these deposits were shown in Figure 6. As is the case for deposits obtained from plating baths with different amounts of tellurium in the bath the crystal structure of the deposits changes with the deposition potential. Refined patterns are shown in Figures S8, S11 and S12. Deposition at $-1.5$ V (W-1.5 V) resulted in a Te-rich composition with significant elemental Te and the longer c-axis phase resembling Sb$_2$Te$_3$ that was also observed in the more Te-rich compositions described above. Lattice parameters for these samples are provided in Figure 10. At $-1.75$ V (W-1.75 V) the intensity of the reflections due to the Sb$_2$Te$_3$-type phase became much stronger and both lattice parameters shortened. This lattice parameter change continued at $-2$ V (W-2 V), with no elemental Te observed and the reappearance of the Sb-type phase that was also seen in the Te-poor phases in the variable concentration studies.

The structures observed after the annealing process are strongly dependent on the composition of the deposit. Te-rich deposits generally show the presence of elemental Te, and two Ge-Sb-Te phases are
observed in proportions that vary consistently with the amount of Te present. However, it has not been possible to pin down precise compositions of these phases as the lattice parameters of the alloys in the literature does not vary as systematically with composition as might be hoped. However, Sb and Te individually deposit as crystalline phases under similar conditions,20 so the deposition of amorphous material does suggest alloying at the deposition stage. The segregation into a mixture of phases during annealing is consistent with the behavior of sputtered Ge₂Sb₂Te₅.

Conclusions

A non-aqueous plating bath for the electrodeposition of ternary GeSbTe solid state phase change random access memory materials is presented. GeSbTe alloys plate amorphously and it is possible to accurately control the average atomic ratio of the deposit by adjusting the precursor ratio, the precursor concentrations, the deposition potential and the thickness of the deposit. In addition to their effect on the composition of the deposits the precursors also affect the morphology: an increase in the tellurium precursor concentration causes the formation of crystalline tellurium clusters on the amorphous GeSbTe deposit, an increase in the germanium precursor concentration acts as a leveler on the morphology of the deposits. The as-deposited GeSbTe alloys are mostly amorphous apart from the presence of crystalline tellurium clusters found in some cases. Upon annealing, the GeSbTe phases are formed.

Based on the results presented here, a strategy to prepare GeSbTe deposits with a desired average atomic ratio was developed: initially the correct Ge:Sb ratio is evaluated by varying the [NBun₄][GeCl₅] and [NBun₄][SbCl₄] concentrations. Subsequently the [NBun₄][TeCl₆] concentration is adjusted to define the tellurium content in the deposit in order to obtain the desired composition. This approach makes use of the fact that the ratio of Ge to Sb in the films is unchanged with the inhomogeneities through better understanding of the nucleation process.

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