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Originally published:
March 2016


DOI: https://doi.org/10.1063/1.4943788

Perma-Link to Publication Repository of HZDR:
https://www.hzdr.de/publications/Publ-25014
Ge-doped GaSb thin films with zero mass density change upon crystallization for applications in phase change memories

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(Received 19 November 2015; accepted 28 February 2016; published online 11 March 2016)

In order to optimize materials for phase change random access memories (PCRAM), the effect of Ge doping on Ga-Sb alloy crystallization was studied using combined in situ synchrotron x-ray techniques, electrical measurements, and static laser testing. The present data emphasize that the crystallization temperature can be increased up to 390 °C with subsequent higher thermal stability of the amorphous phase; phase segregation is evidenced with GaSb, Sb, and Ge phases that crystallize in a two-step crystallization process. The Ge-doped GaSb films exhibit a larger electrical contrast as compared to undoped GaSb alloy (up to ×100). The optical contrast measured by laser testing is shown to follow the mass density change variations upon crystallization, with a negative contrast (higher value in amorphous state) whatever Ge-doping levels. In situ x-ray reflectivity measurements show that zero mass density change can be achieved by low Ge-doping. Ge-doped GaSb alloys look promising since a phase change material with zero mass density change and higher crystallization temperature satisfactorily fulfills the specifications for reliable PCRAM cells in terms of endurance and data retention. © 2016 AIP Publishing LLC.

Phase change random access memories (PCRAM) belong to the most mature emerging memory technologies.1 Mainly driven by smart phone and nomad applications, PCRAM products at the 45 nm node have been manufactured.2 This technology relies on the possibility to repeatedly switch the phase of a phase change material (PCM) within very short times (few nanoseconds) between its amorphous and crystalline states. PCMs are characterized by a unique combination of properties:3 huge electrical and optical contrasts are observed between amorphous and crystalline states, the amorphous phase exhibiting in general high electrical resistivity and low optical reflectance.4,5 Most of fabricated PCRAMs integrate PCM compounds based on the Ge2Sb2Te5 (GST) alloy first introduced for optical storage applications.6 Despite its remarkable properties, GST exhibits however a quite poor high temperature data retention due to its low crystallization temperature (≈150 °C), and a relatively high change in mass density upon switching (about 7%).6 These two features limit the use of GST for several embedded system or automotive applications and lead to void formation and subsequent failures in PCRAM cells.7–9 Other PCM alloys including doped-GST2 or GeTe1−xSbx10 with improved phase change memory performances are studied, and few of them such as GeTe-CuTe11 exhibit no volume change explained by a two-step crystallization. Because of their high thermal stability,12 long data retention,13,14 fast switching,14 the Te-free Ga1−xSbx alloys were proposed as potential candidates for PCRAM applications with their unusual crystallization behavior.15 The stoichiometric GaSb alloy shows actually negative optical contrast (higher optical reflectance in the amorphous state)16 associated with a decrease in mass density upon crystallization.17 By increasing the Sb content in Ga1−xSbx alloys up to 91 at.% Sb, no change in mass density nor in film thickness was evidenced in the Ga0.3Sb0.7 material.17 However, increasing Sb ratio in Ga-Sb alloy decreases the crystallization temperature (Tx) and leads to Sb segregation.18 In this context, the main objective of the present study is to tune Ga-Sb alloy composition for (i) combining zero mass density change upon crystallization with a higher crystallization temperature and (ii) improving both data retention and cyclability for memory applications.5

We have studied the effect of Ge doping on Ga-Sb alloy crystallization using combined in situ synchrotron x-ray techniques and electrical measurements (Rs). Ge-doping was previously used to enhance the thermal stability of GST material:18 it was shown that optimization of the programming technique allows to boost the SET speed of such PCM by overcoming the decrease of crystallization speed caused by Ge enrichment.19 The pseudobinary GaSb-Ge system has a simple equilibrium phase diagram with eutectic and two phase equilibria in the solid state, GaSb and Ge. Quenching from the melt results in the formation of a metastable solid solution over the entire concentration region.20

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[http://dx.doi.org/10.1063/1.4943788]
Thin films (50 nm thick) of Ge-doped GaSb were prepared on 500 nm SiO₂/Si(100) substrates by DC magnetron co-sputtering technique from a compound Ga₀.₄₅Sb₀.₅₅ target and pure Ge targets. The film composition was controlled by Rutherford Backscattering Spectrometry (RBS) with an error of ±0.5 at.%. Films with three different Ge concentrations were fabricated, referred as low-, medium-, and high-Ge doping level in the following (for intellectual property protection reasons, exact Ge doping cannot be disclosed). A set of samples were capped with 10 nm thick SiO₂ layer to prevent any evaporation upon heating. Combined in situ x-ray diffraction (XRD), x-ray reflectivity (XRR), and sheet resistance measurements (Rs) were performed using a dedicated vacuum chamber on the BM20B-Rosendorf beamline at European Synchrotron Radiation Facility (ESRF) in Grenoble, France, using an incident photon energy of 11.5 keV (λ = 1.07 Å), and a 1D Mythen detector (see Ref. 15 for experimental details). XRD, XRR, and Rs measurements were simultaneously performed, while the sample was annealed with a constant heating rate of 2 °C/min, from room temperature up to 500 °C. XRD patterns were recorded in grazing incidence (θ = 1°). Finally, the optical contrast was investigated using a custom-built static laser tester.

Fig. 1 shows the sheet resistance evolution as a function of temperature for the capped layers. The samples are initially prepared on 500 nm SiO₂/Si(100) substrates by DC magnetron co-sputtering technique from a compound Ga₀.₄₅Sb₀.₅₅ target.

![Graph showing sheet resistance for Ge-doped Ga-Sb alloys with variable Ge-doping level as a function of temperature for a heating ramp at 2 °C/min to 500 °C and subsequent cooling to room temperature. The black arrow indicates a possible two-step crystallization process for the highly Ge doped GaSb.](image)

**FIG. 1.** Sheet resistance for Ge-doped Ga-Sb alloys with variable Ge-doping level as a function of temperature for a heating ramp at 2 °C/min to 500 °C and subsequent cooling to room temperature. The black arrow indicates a possible two-step crystallization process for the highly Ge doped GaSb.

Electrical contrast was derived from the ratio of Rs measured at room temperature before (RSbefore) and after annealing (RSafter). It is clearly demonstrated that Tₓ increases with increasing Ge-doping, whereas the resistance in the amorphous state (Rx) decreases. The medium Ge-doped alloy exhibits the highest electrical contrast and a two-step resistance drop is clearly detectable for the highest Ge-doping level (see black arrow), indicating possible two-step crystallization.

### Table I. Summary of microstructural, electrical, and optical properties of Ge-doped GaSb films. Tₓ corresponds to the crystallization temperature deduced either from the drop in Rs or the appearance of diffraction peaks in XRD. Tₛ is the Ge phase crystallization deduced from XRD. aₐm is the relative variation of the crystalline GaSb cell volume for Ge-doped layer compared to undoped layer. \( \frac{a_{\text{crystalline}} - a_{\text{amorphous}}}{a_{\text{amorphous}}} \). The electrical contrast is defined as \( \frac{R_s^{\text{crystalline}}}{R_s^{\text{amorphous}}} \), where \( R_s^{\text{amorphous}} \) and \( R_s^{\text{crystalline}} \) are the reflectance for amorphous (as-deposited, before the write pulse) and crystalline phase after the write pulse, respectively.

<table>
<thead>
<tr>
<th>Ge doping level</th>
<th>Tₓ (°C)</th>
<th>Tₛ (°C)</th>
<th>aₐm (Å)</th>
<th>XRD (%)</th>
<th>Electrical contrast</th>
<th>Density change</th>
<th>Optical contrast</th>
</tr>
</thead>
<tbody>
<tr>
<td>Undoped (Ref. 23)</td>
<td>226</td>
<td>220</td>
<td>...</td>
<td>6.138</td>
<td>...</td>
<td>2.4 x 10²</td>
<td>-5.2 ± 0.5</td>
</tr>
<tr>
<td>Low</td>
<td>374</td>
<td>379</td>
<td>407</td>
<td>6.053</td>
<td>-4.1</td>
<td>2.7 x 10³</td>
<td>-0.3 ± 0.1</td>
</tr>
<tr>
<td>Medium</td>
<td>384</td>
<td>388</td>
<td>411</td>
<td>6.055</td>
<td>-4.0</td>
<td>3.7 x 10³</td>
<td>-2.5 ± 0.2</td>
</tr>
<tr>
<td>High</td>
<td>390</td>
<td>397</td>
<td>410</td>
<td>6.047</td>
<td>-4.4</td>
<td>5.5 x 10³</td>
<td>-1.6 ± 0.2</td>
</tr>
</tbody>
</table>
appears at $T_{Ge}$ (see Figs. 2 and 3). Considering that the solubility of Ge in GaSb is less than 2 at.\% around 400°C (Ref. 27), this initial crystalline phase could correspond to a strained GaSb phase. Actually, the average 2θ position of these 3 broad peaks (18.12°, 29.93°, and 35.16°) could correspond, respectively, to the (111) (2θ = 17.55°), (220) (2θ = 28.85°), and (311) (2θ = 33.98°) theoretical Bragg peak positions of GaSb shifted towards higher 2θ angles. This hypothesis is supported by the fact that the mass density of undoped GaSb film is known to decrease upon crystallization producing an expansion of the layer volume.23 The Ge atoms introduced in Ge-doped GaSb could block this volume expansion resulting in a strained GaSb layer under compressive stress with the 2θ positions shifted towards higher angles, indicating interplanar spacing smaller than the relaxed ones. Following this hypothesis, the first crystalline GaSb domains would be surrounded by both Ge and Sb atoms (due to the slight excess of Sb contained in the film15), Ge and Sb elements form a binary phase diagram with only an eutectic point, very low solubility of Sb (Ge) in Ge (Sb), and two separated phases Sb and Ge in thermodynamically stable conditions.28 Moreover, (i) different types of metals are known to reduce the crystallization temperature of Ge and those that form an eutectic with Ge are the most effective29 and (ii) Sb is known to have an explosive crystallization. Consequently, the small excess of free Sb could promote Ge crystallization (and thus Sb crystallization as Sb is not soluble in Ge) at $T_{Ge}$, i.e., when Ge-Sb bonds are broken upon thermal annealing. Due to the Ge and Sb phase crystallization, larger crystalline GaSb grains and domains could form at the same temperature ($T_{Ge}$) allowing sharper GaSb diffraction peaks to appear at a more relaxed 2θ position as measured on XRD patterns after annealing. The co-sputtering allows deposition of metastable films that have a uniform distribution of Ga, Sb, and Ge, but subsequent heating provides the energy to move the system toward equilibrium by phase segregation. Such results and hypothesis point out that knowing the short range order and bonding in such alloy is a key parameter to understand the crystallization process.

To follow density and thickness change, in situ XRR patterns were recorded simultaneously to XRD and Rs measurements. As in situ XRR patterns show minor changes upon annealing, we focus only on the XRR patterns before (amorphous phase) and after annealing (crystalline phase) for the three Ge-doping levels (shown in Fig. 4). Contrary to most PCMs, the undoped GaSb exhibits an decrease in mass density leading to an increase in film thickness upon crystallization.17,23 The results deduced from XRR are summarized in Table I. At any Ge-doping level, a negative mass density change upon crystallization is observed. Particularly, the low Ge-doped sample exhibits no significant change upon annealing (mass density change estimated to −0.3%). As already described in a previous study,30 a fast Fourier transform (FFT) algorithm was applied on the series of in situ recorded XRR patterns and confirmed the results: no change in the layer thickness was detected upon crystallization for the low Ge-doped GaSb film using this method.

In addition, the change in optical reflectance $\frac{R_{opt}}{R_{opt}}$ was deduced from laser testing. The write pulse was selected in power and energy such that it led to full crystallization of the amorphous, as-deposited film, but no ablation. The results are summarized in Table I: the negative contrast is confirmed for all samples. Moreover, the optical contrast deduced from laser testing matches very well the mass density variations deduced from XRR upon crystallization. Ge-doping is actually shown to reduce the optical contrast, the lowest optical contrast being measured for low Ge-doping film that exhibits no mass density change. For medium Ge-doping film, both the optical contrast and the mass density variation increase as compared to low and high Ge-doping levels. These experimental results tend to confirm a correlation between the mass density change and the magnitude of the optical contrast between the amorphous and crystalline states. As shown by Detemple et al.,31 and confirmed by Saito et al.,32 an approximately linear relationship links the optical contrast and the density change in many PCMs, for both positive and negative changes upon crystallization.

To correlate structural parameters measured by XRD and mass density change deduced from XRR, the average lattice parameter of the crystalline GaSb phase ($a_{GaSb}$ in Table I) in the Ge-doped GaSb layers was calculated from (111), (220), and (311) Bragg reflections of the ex situ XRD patterns. The average volume of the GaSb cell was also calculated for each Ge-doped layer and compared to the one measured in undoped GaSb layer: the values of $\frac{V_{GaSb}}{V_{GaSb}}$ are...
reported in Table I. At any doping level, the GaSb lattice parameter is smaller in Ge-doped layer compared to undoped layer: the average volume reduction is about $-4\%$, meaning that the crystalline GaSb phase has a smaller volume in Ge-doped GaSb layers than in undoped GaSb layer. Supposing that the GaSb phase has the same number and type of atoms per cell in Ge-doped and undoped GaSb layers (consistent with the observed phase separation), this calculation shows that the mass density of the GaSb crystalline phase is higher in Ge-doped GaSb than in undoped GaSb layer. This is consistent with the smaller density variation measured by XRR upon crystallization for Ge-doped layers, the density of the crystalline GaSb phase being less reduced than in undoped GaSb, thus contributing to smaller changes in the density of the whole layer upon crystallization. Stress effects appear consequently as an important issue to understand mass density change upon crystallization for doped GaSb layers.

Finally, considering materials requirements for PCRAM devices, the addition of dopants which increase $T_x$ usually leads to a reduction of the write current and an improved retention time of the amorphous phase, but reduces nevertheless the crystallization speed.\cite{19} For Ge-doped GaSb PCM, it has been shown that the devices can still be SET within 100 ns even if $T_x$ is high.\cite{33} That is one of the unique characteristics for GaSb based material since it can have high thermal stability without sacrificing speed. The phase segregation observed in this paper could, however, be a key issue for device performance as it can affect crystallization. Even so, the cycling endurance in the Ge-doped GaSb devices is guaranteed to up to $1 \times 10^8$.\cite{33} It should actually be pointed out that the experimental conditions (slow ramp rate and long annealing time) for the combined experiment could favor Ge crystallization and phase separation as they correspond to high thermal budget and do not relate to thermal budget involved during the device SET process.

The present data emphasize that material engineering enables advantageous tailoring the properties of GaSb alloy for PCRAM applications. By doping the stoichiometric GaSb compound with Ge, the crystallization temperature can be increased up to $390\,^\circ\text{C}$ with subsequent higher thermal stability of amorphous phase, specification required for improving data retention. Moreover, our study shows that zero mass density change can be achieved by low Ge-doping, consequently reducing void formation upon switching and preventing failures during cycling. XRR and XRD analysis shows that the reduction in mass density change upon crystallization is associated with a smaller cell volume of the crystalline GaSb phase in Ge-doped layers, and the optical contrast measured by laser testing is shown to follow the mass density variations upon crystallization. However, phase segregation is clearly evidenced: three phases, namely, GaSb, Sb, and Ge, crystallize in a two-step crystallization process. When such phase change material is integrated in a PCRAM cell, such two-step crystallization may be advantageously used for multi-level

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3.png}
\caption{(a) XRD patterns ($\lambda = 1.07\,\text{Å}$) recorded before annealing, at $T_x$, and after annealing on medium 50 nm thick Ge-doped GaSb layer. The vertical markers represent the theoretical Bragg reflections for GaSb, Sb, and Ge phases. The numbers 1, 2, and 3 correspond, respectively, to the GaSb (111), (220), and (311) theoretical Bragg reflections; (b) in situ XRD analyses of medium and high Ge-doped GaSb layers recorded during heating ramp at 2 $^\circ\text{C/min to 500}\,^\circ\text{C}$.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig4.png}
\caption{XRR patterns ($\lambda = 1.07\,\text{Å}$) recorded on amorphous (black) and crystalline (red) state on the Ge-doped GaSb layers. In each figure, the inset corresponds to a zoom in on the total reflection edge region of the XRR patterns before and after annealing.}
\end{figure}
data storage if related to two unambiguously discriminated resistance states, as shown for Ga$_{19}$Sb$_{81}$ alloy.\textsuperscript{12} Both XRR and XRD results emphasize that upon Ge-doping stress effect as well as short range order and bonding may play a key role to understand the crystallization process. Regarding electrical properties, Ge-doped GaSb alloy exhibits a larger electrical contrast as compared to undoped GaSb alloy (up to $\times 100$). As conclusion, the results obtained on Ge-doped GaSb alloys look promising since a PCM alloy with zero mass density change and higher crystallization temperature satisfactorily fulfills the specifications for reliable PCRAM cells in terms of endurance (cycling) and data retention. The European Synchrotron Radiation Facility is also acknowledged for supplying synchrotron radiation facilities.