Thermal conductivity of carbon doped GeTe thin films in amorphous and crystalline state measured by modulated photo thermal radiometry

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Abstract. The thermal conductivity and thermal boundary resistance of GeTe and carbon doped GeTe thin films, designed for phase change memory (PCM) applications, were investigated by modulated photo thermal radiometry. It was found that C doping has no significant effect on the thermal conductivity of these chalcogenides in amorphous state. The thermal boundary resistance between the amorphous films and SiO₂ substrate is also not affected by C doping. The films were then crystallized by an annealing at 450°C as confirmed by optical reflectivity analysis. The thermal conductivity of non-doped GeTe significantly increases after crystallization annealing. But, surprisingly the thermal conductivity of the crystallized C doped GeTe was found to be similar from that of the amorphous state and independent of C concentration. As for the amorphous phase, C doping does not affect the thermal boundary resistance between the crystalline GeTe films and SiO₂ substrate. This behaviour is discussed thanks to XRD and FTIR analysis. In particular, XRD shows a decrease of crystalline grain size in crystalline films as C concentration is increased. FTIR analysis of the film before and after crystallization evidenced that this evolution could be attributed to the disappearing of Ge-C bonds and migration of C atoms out of the GeTe phase upon crystallization, limiting then the growth of GeTe crystallites in C-doped films.

1. Introduction

Phase Change Memories (PCM) are recognized as the next-generation of non-volatile memories thanks to their fast, nanosecond timescale read/write speed, good scalability leading to high data storage capacity and low power consumption [1]. PCM cell is based on nanoscaled volume of a phase change (PC) material which is generally a Te-based chalcogenide alloy. The heating of the PC material permits a reversible switch between its amorphous and crystalline states which have very different electrical resistivity and thus can be exploited for binary data storage. In the PCM device, crystallization of the PC material is realized by heating of the amorphous PC alloy above its crystallization temperature by electrical current pulses (SET), while amorphization (RESET) is achieved by melting and quenching of the crystalline region with higher and shorter electrical current pulses than in SET operation. The most common PC chalcogenide alloy is Ge₂Sb₂Te₅ (GST). It has been extensively studied for years for optical data storage due to its fast transition rate and high cyclability [2]. For current PCM applications, one of the most limiting parameter of GST is its low
crystallization temperature (∼150°C), guaranteeing data retention up to 10 years at 75°C only, which is not enough for fulfillment of embedded applications requirements (mobile, automotive…). For this reason, numerous research works are carried out in order to develop new materials for improving the PCM performance. Two main issues have to be addressed: the improvement of the stability of the amorphous phase to increase the data retention performances, and the reduction of current needed for RESET operation in PCM devices in order to limit the programming energy. In that context, doping of GST PC material with carbon, nitrogen or silicon, for tuning its physical properties has received increasing attention [3][4]. Moreover, GeTe, whose crystallization temperature is about 180°C, was investigated as an alternative for GST [5][6]. Promising effects of doping GeTe with carbon or nitrogen for PCM applications were also reported [7][8][9][10]. In particular, doping of GeTe with carbon atoms significantly increases its crystallization temperature above 180°C, leading to more stable amorphous state and thus improving the data retention properties in PCM devices. Furthermore, the introduction of C in PC material is shown to significantly reduce the RESET current with respect to pure GeTe and GST, making it a good candidate to address the major issues of PCM technology.

While the effect of carbon doping on electrical properties of GeTe has been widely investigated, no data has been reported on its influence on the thermal conductivity. The thermal design is a key point in PCM devices as the switching between SET and RESET state is based upon heat dissipation from Joule effect in the active area of the chalcogenide. Furthermore, the thermal interference between neighboring cells (also called thermal cross-talk) is a phenomenon that can lead to the undesirable switching of cells. The control of thermal cross-talk is of major importance to the scalability of PCM technology. As demonstrated in [11], the temperature field in PCM cell is affected not only by the thermal conductivity of the chalcogenide, but also greatly by the thermal boundary resistance (TBR) between the chalcogenide and its contiguous layers. The TBR plays a significant role in confining the heat flux as its values are comparable with the thermal resistance of the chalcogenide layer itself.

For this reason, in this work we studied the influence of carbon doping on the thermal properties of GeTe thin films in amorphous and crystalline states. The thermal conductivity of undoped and C-doped GeTe thin films and the thermal boundary resistance with their surrounding layers were determined by Modulated Photo Thermal Radiometry (MPTTR). The obtained results were correlated with the analysis of the structural properties according to doping concentration before and after crystallization. In a first part, details of the experimental techniques used for sample preparation and characterization are presented. Then, in a second section, the obtained results will be presented and discussed.

2. Experimental details

2.1. Sample preparation

Amorphous GeTe and C-doped GeTe films (with thicknesses of 100, 200, 300 and 400 nm for each composition) were deposited by magnetron sputtering in an Ar atmosphere on 200 nm silicon wafers covered by a 500 nm thick SiO2 top layer. C-doped samples were prepared by co-sputtering of GeTe and C targets. The concentration of C in doped films was varied by changing the sputtering powers applied to GeTe and C targets and three C doping concentrations were prepared: 10 at.%, 15 at.%, 20 at.%. The chemical composition of the deposited layers were measured by Rutherford Back Scattering (RBS) for the Ge and Te, and Nuclear Reaction Analysis (NRA) for C dopant. The thicknesses of the deposited films as well as their homogeneity were controlled by X-Ray Reflectivity (XRR).

A subset of both doped and undoped samples in crystalline phase was prepared by thermal annealing at 450°C for 15 min directly in the deposition vessel. As reported in [12], by optical reflectivity measurement, this annealing permits thus to obtain a stable crystalline state of the films since the crystallization temperatures are 180, 310, 350 and 370°C for GeTe films with 0, 10, 15 and 20% of C concentration respectively. All amorphous and crystalline films were then covered by sputtering of an additional 100 nm thick layer of platinum, acting as a thermal and optical transducer.
for MPTR measurements. A schematic view of the layered sample cross section is represented in Figure 1.

![Schematic representation of the studied sample cross section. Symbol $e_i$ denotes the thickness of the layer $i$.](image)

Figure 1. Schematic representation (not to scale) of the studied sample cross section. Symbol $e_i$ denotes the thickness of the layer $i$.

2.2. Modulated Photo Thermal Radiometry (MPTR)

The experimental details of our Modulated Photo Thermal Radiometry (MPTR) setup have been presented elsewhere [13]. The main principle consists in front face periodic heating of the studied sample by a laser source. In order to control the laser absorption by the sample, a 100 nm thick platinum layer is deposited by sputtering in order to act as an optical and thermal transducer. Indeed, the heat flux is absorbed by the Pt layer due to its high extinction coefficient at the laser wavelength (1064 nm). On the other hand the Pt layer is assumed to be isothermal for all the frequency range swept during the experiment. The thermal response of the sample is measured using an infrared detector. As the heating rate is low, the linearity assumption of heat transfer is fulfilled and the emitted infrared radiation from the sample surface is linearly proportional to its temperature. The measured data are amplitude and phase of detector signal as a function of frequency. The thermal properties are thus obtained by fitting of the experimental phase by mean of a thermal model which allows to describe the carried out experiment [13]. According to the film thicknesses and modulation frequency, the transient behaviour fully fulfils the Fourier regime of heat conduction. Since the heated area is much larger (laser spot of 2 mm in diameter) than the film thickness, the one-dimensional heat transfer is considered. The explored frequency range in our experiment is 1-10 kHz. The penetration of heat is thus much larger than the film thickness according to relation $d = \sqrt{\alpha/\pi f}$ where $\alpha$ is the thermal diffusivity of the film and $f$ is the frequency. Therefore, the films can be viewed as the thermal resistances and the Si substrate behaves as a semi-infinite wall. In this way the MPTR allows measuring the thermal resistance $R_{th}$ of the layered stack defined as (assuming the thermal resistance of the Pt layer is negligible):

$$R_{th} = \frac{R_{Pt/GeTe} + e_{GeTe} + R_{GeTe/SiO_2} + e_{SiO_2} + R_{SiO_2/Si}}{R_t}$$

(1)

In this relation $R_{a/b}$ denotes the thermal resistance at the interface between layers $a$ and $b$, and $e_{SiO_2}/k_{SiO_2}$ is the thermal resistance of the SiO$_2$ layer, which can be subtracted, since $k_{SiO_2} = 1.45$ Wm$^{-1}$K$^{-1}$ value is known from the literature [13]. Furthermore, the very low resistance $R_{SiO_2/Si} = 4.5 \times 10^{-9}$ m$^2$KW$^{-1}$ is also subtracted from $R_{th}$ [14]. By performing measurements on thin films with 4 different thicknesses and assuming that the thermal resistance at the interfaces is the same for all the samples, it is then possible to estimate the intrinsic out-of-plane thermal conductivity of the film (which is assumed to be constant whatever the film thickness) and the thermal resistance at the interfaces. By plotting the thermal resistance $R_t$ as a function of the thickness $e_{GeTe}$ of the considered GeTe film, we can extract the thermal conductivity $k_{GeTe}$ as the inverse of the slope of $R_t$. By extrapolation to $e_{GeTe} = 0$, we can directly deduce the thermal resistance of the interfaces TBR.
Experiments have been repeated three times and discrepancy between the measured data was always found lower than the measured standard deviation. In order to increase the signal to noise ratio, all the measurements were carried out at 100°C, in argon atmosphere in order to prevent oxidation, inside a commercial furnace.

2.3. FTIR spectroscopy
The study of the vibrational bonds modes of non-doped and C-doped GeTe films was performed by Fourier-Transform InfraRed (FTIR) spectroscopy. FTIR spectra in transmission mode of different samples were acquired with BIO-RAD QS500 and Brucker VERTEX 80V FTIR spectrometers in order to cover 50 to 400 cm$^{-1}$ (low frequency - LF) and 400 to 2000 cm$^{-1}$ (high frequency - HF) ranges. The absorbance spectra of substrate used for thin films deposition have been also measured prior to deposition in order to remove substrate contribution from the absorbance spectra of GeTe thin films.

3. Results and discussion
The MPTR measured thermal resistances of all compositions of GeTe layers, according to the layer thickness, in amorphous and crystalline states, are presented in Figures 2 and 3 respectively. Concerning pure GeTe, the densification of material upon the crystallization was taken into account, according to data reported in [15]. As no data is available for C doped GeTe, the crystalline doped layers thicknesses were kept at nominal as deposited values since it has been reported that C-doping largely reduce the density change upon crystallization for GST [16]. As shown in Figures 2 and 3, the thermal resistance of the films exhibits a linear dependence with film thickness indicating that in studied layers the heat conduction respects Fourier's law. In fact, the mean free path of phonon and electron in GeTe, evaluated to be inferior to 10 nm [9], is much shorter than minimal thickness of the measured film. Following the above, a reliable estimation of the thermal conductivity $k$ and the thermal boundary resistance TBR, could be done.

![Figure 2](image_url)

**Figure 2.** Measured thermal resistances of undoped and C-doped GeTe thin films in amorphous state.

![Figure 3](image_url)

**Figure 3.** Measured thermal resistances of the undoped and C-doped GeTe thin films in crystalline state after annealing at 450°C for 15 min.

The values of both $k$ and TBR obtained for as deposited and crystallized samples are summarized in Table 1. The standard deviations associated with the reported values are related to the uncertainty of the linear fits of the data in Figures 2 and 3.
Table 1. Estimated thermal conductivity $k$ and thermal boundary resistance TBR for both amorphous and crystalline, non-doped and C doped GeTe thin films.

|                | Amorphous | Crystalline |
|----------------|-----------|-------------|
|                | GeTe      | GeTeC10%    | GeTeC15%    | GeTeC20%    |
| $k$ [Wm$^{-1}$K$^{-1}$] | 0.22±0.02 | 0.19±0.01   | 0.19±0.01   | 0.19±0.01   |
| TBR [10$^8$ m$^2$KW$^{-1}$] | 22.6±7.2  | 20.8±5.6    | 21.4±5.4    | 18.5±7.1    |

Figure 2 shows that the thermal resistances of pure undoped and C doped GeTe layers, regardless the C concentration, are very similar when films are in as-deposited amorphous state. Figure 3 shows that the thermal resistance of pure GeTe films significantly decreases upon crystallization, indicating that its intrinsic thermal conductivity increases from 0.22 Wm$^{-1}$K$^{-1}$ to 3.10 Wm$^{-1}$K$^{-1}$. These values are in very good agreement with literature data, obtained on GeTe thin films by $3\omega$ method [9]. The observed variation can be related to the large increase of long range order in the crystalline phase compared to disordered amorphous phase leading to a better phonon propagation in the crystalline phase. Nevertheless, for C-doped GeTe layers, the thermal resistances exhibit no significant evolution between the amorphous and crystalline phases and this regardless the C concentration. This observation evidences that the intrinsic thermal conductivity of crystalline C doped GeTe layers is very low (around 0.21 Wm$^{-1}$K$^{-1}$) compared the pure undoped crystalline GeTe layer (3.10 Wm$^{-1}$K$^{-1}$), and is very similar than values found for the amorphous phases (0.19 Wm$^{-1}$K$^{-1}$). The observed phenomenon of decrease of thermal conductivity in GeTe films by C incorporation is in accordance with results obtained on C-GST and N-GeTe [3][9], and can be attributed to higher, due to dopant-induced impurities, phonon scattering rate in doped materials.

From our measurements, the resulting TBR were found in the range of a few tens of 10$^8$ m$^2$KW$^{-1}$ for all materials. These values are consistent with literature [9][13]. The negative value for GeTeC10% has no physical meaning. The associated standard deviation, higher than value itself, indicates that the TBR for this sample could be very low. The highest TBR value was found for GeTeC15%. The effect of C doping on the TBR could not be distinguished since the associated standard deviation corresponds to 68% confidence interval.

In order to understand the origin of the different thermal conductivity found in GeTe and C-GeTe, physico-chemical analysis was performed. XRD measurements (insert of Figure 5) were carried out on annealed crystalline samples of each composition in order to analyze the crystalline phase of the films. As already reported [7], C-doped GeTe films with a carbon content lower 10 at. % crystallize mainly in the rombohedral structure at room temperature, like in pure GeTe. But for C concentration higher than 10 at.%, the GeTe crystalline phase is more and more cubic with a progressive dissapear of the (104)/(110) doublet of the rombohedral structure in favor of one unique (220) peak relative to the cubic phase of GeTe [17]. From the diffraction diagrams, the size of crystallite in the different samples could be evaluated by calculation from the diffracted peak width of the Diffractive Coherent Domain (DCD) using the Scherrer formula. However, evaluation of DCD, sensitive to structural imperfections and instrumental abberations, is not an absolut value of the crystallite size but should only be used for comparison between the doped and un-doped samples.
In Figure 4 is plotted the change of crystallite size in undoped GeTe film as a function of the annealing temperature. It can be noticed, that the grain size increases with increasing annealing temperature, starting from around 40 nm just after crystallization at 175°C up to 165 nm for GeTe film annealed at 450°C. In Figure 5 are also plotted the changes in crystallite size according to C concentration for GeTe films annealed at 450°C. As it is clearly evidenced by Figure 5, the size of crystallites is significantly much lower in C doped films than in pure GeTe, and decreases as the C concentration is increased. Similar effect was observed in [4] when GST was doped with carbon. However, the crystallite size found in C-GST was much lower than in our C-GeTe, which is around 20 nm in 20% C content GeTe.

FTIR spectroscopy on both C-doped and undoped GeTe has been performed on as-deposited and crystallized samples, in order to get more insight about any possible change in local atomic bonding configuration upon annealing. Low frequency (LF) and high frequency (HF) spectra for amorphous and crystallized GeTe films are represented in Figure 6 a) and b) respectively. The spectra obtained on amorphous as-deposited materials (dotted lines) have been already discussed in [12][18]. In HF range around 600 cm⁻¹ and 1750 cm⁻¹, the absorption peaks which are increasing as the C content is increased, are attributed to the apparition of C-Ge/C-Te bonds and also of C-C- bonds, respectively [19]. At the same time, in LF range, the vibrational absorption band around 150 cm⁻¹ progressively decreases when C is incorporated in a-GeTe. The above effect is the result of an increased mechanical rigidity of C-doped chalcogenides, leading to a more stable amorphous structure, and explain the reported increase of crystallization temperature [12].

The absorption spectra acquired on crystalline GeTe samples exhibit a depletion of LF vibrational modes (80 and 125 cm⁻¹ peaks in pure GeTe) upon C addition in GeTe concomitant to a dissapear of the HF absorption peaks related to C-Ge/C-Te and short C-C- bonds in C-GeTe upon crystallization. It indicates, that C-Ge bonds dissapear in the crystalline phase of C-GeTe and that C atoms can migrate out of GeTe phase probably to grain boundaries, limiting therefore the growth of crystallites. This last result is consistent with the evolution of grain size estimated from XRD diagrams. Finally, from such observations, one can draft here a preliminary conclusion on the origin of the decrease of thermal conductivity in crystalline C-GeTe films compared to pure GeTe. As a result, the decrease of crystallite size in GeTe with C content will result in an increase of phonon scattering rate by the presence of C impurities at grain boundaries leading to a lower thermal conductivity in crystalline C-GeTe compared to pure crystalline GeTe films [20][21].
Figure 6. FTIR absorbance spectra of GeTe and C doped GeTe: a) low frequency; b) high frequency. Dotted line corresponds to amorphous phase; full line corresponds to 450°C annealed crystalline phase.

The results obtained in this work can be directly related to the investigations on RESET current reduction in C-GeTe based PCM devices [7][8]. In fact, the previous observed decrease of RESET current when doping GeTe with C can be linked to the decrease of $k$ in crystalline C-GeTe and therefore increase of Joule effect heating by an improved thermal confinement of the active phase change material volume in the PCM cell.

4. Conclusion
The effect of carbon doping on the thermal conductivity of GeTe thin films designed for phase change memory was investigated. The thermal conductivity of C doped and undoped GeTe thin films was measured by modulated photo thermal radiometry. The thermal boundary resistance at the interfaces of the films was also estimated. It was found that C doping does not affect significantly the thermal conductivity of GeTe in the amorphous phase. The thermal boundary resistance was also found not affected by incorporation of C in GeTe, for both, amorphous and crystalline phases. Nevertheless, this study evidences a significant effect of C doping on the thermal conductivity of crystalline GeTe films. In particular, the introduction of C in GeTe is at origin of a large decrease of its thermal conductivity in crystalline state. This effect has to be related to the drastic reduction of crystallite size in C-GeTe due to segregation of C-impurities at grain boundaries upon crystallization resulting in a higher phonon scattering rate. Finally, this result can be obviously related to the reduction of amorphization RESET currents in phase change memory devices thanks to a more efficient Joule heating effect due to an improved thermal confinement of the active volume in the phase change memory cell.

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