

EFFECT OF DOPANT INCORPORATION IN PHASE CHANGE MATERIAL

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ABSTRACT

Phase change memory (PCRAM) technology is considered to be one of the most promising alternative technologies for non-volatile embedded resistive memories (RRAMs) [1]. Chalcogenide phase change materials (PCMs), such as GeTe and Ge_xSb_yTe_z (GST), are excellent candidates thanks to their rapid phase transformation (tens of ns) between amorphous and crystalline states and to the large variation of resistivity between the two states. In PCRAM devices, the transition from low to high resistivity state is obtained by phase transformation of the PCM, from crystalline to amorphous, by applying a short and high current pulse that locally melts and amorphizes the material. The material is then locally recrystallized by a longer and lower pulse. Memories based on PCMs offer high scalability, fast programming and good cyclability. To allow operation at relatively high temperatures in embedded applications, it is crucial to improve the stability of the amorphous phase. Carbon and nitrogen doping have been shown to significantly increase the crystallization temperature [1-3]. Moreover, the high RESET current requirement [2], which is a limit to the scalability of GeTe and GST, can be reduced by the incorporation of a dopant element [4]. Understanding the effect of dopants on the change of electronic properties and the mechanisms of the phase transformation requires analysis of the local order and structure of the amorphous to crystalline phases. In this context, our recent results on carbon [5] and nitrogen doped amorphous GeTe will be presented. By combining FTIR spectroscopy and *ab initio* molecular dynamics we show that dopants induce a strong modification of the properties of PCMs. Finally, these results will be discussed in relation with phase change properties of such doped PCMs in integrated devices.

Keywords: doping, carbon, nitrogen, amorphous

1. INTRODUCTION

Phase Change Memory is a non-volatile memory (NVM) technology in which the logic states are stored as the low-resistive-crystalline (SET) and high-resistive amorphous (RESET) states of a chalcogenide material, such as Ge₂Sb₂Te₅ (GST) or GeTe. These phase change materials show the unique property to be able to quickly and reversibly switch between an amorphous (A-phase) and a crystalline state (C-phase) that are characterized by very different optical and electrical properties. These properties allow the integration of such chalcogenide materials in optical storage devices (DVD-RAM) and more recently in NVM so called phase change memories (PCMs). Short read and write times, good data-retention and multi-level capability make PCM very attractive for next NVM generation. However, the minimum size of the PCM selector element, and hence the scalability of the PCM technology, could be limited by the high reset current (I_{RESET}) required to switch the phase change material from the SET state to the RESET state. It has been already shown that it is possible to reduce I_{RESET} using oxygen- or silicon-doped GST instead of pure GST. Moreover for embedded applications at relatively high temperature, the stability of the amorphous phase needs to be improved in order to increase the retention time. The retention time corresponds to the temperature/time for which the PCM cell switch from its amorphous to crystalline state and is fixed to 150°C for 10 years in case of embedded applications. GST and GeTe show retention time of about 75°C for 10 years and 110°C for 10 years respectively which are too low for applications. In this context, carbon and nitrogen which can reduce the reset current of memory cells and improve amorphous phase stability can also be an interesting doping solution for PCM in order to attempt these challenges.

Recently, it has been shown that doping GeTe with carbon or nitrogen strongly increases the crystallization temperature T_x accompanied by a beneficial increase of the retention time. Compared to pure GeTe with a T_x of about 180°C, the incorporation of 10 at % of N or C atoms increases T_x up to 260°C and 340°C respectively. Thus, in this paper we investigate the effect of dopant on the local structure of the amorphous phase of C and N-doped GeTe (named a-GeTeC and a-GeTeN), in order to understand the stabilizing effect of C and N doping on a-GeTe phase. By combining total x-ray scattering and *ab initio* simulations, we have shown that C and N strongly modify the amorphous structure of GeTe. Moreover, Fourier-Transform Infrared Spectroscopy (FTIR) and *ab initio* simulations reveal by vibrational modes analysis that the incorporation of C or N dopants drastically affects the mechanical properties of amorphous GeTe which could finally give an explanation to the stabilization of the amorphous phase of GeTe doped with C or N.

2. EXPERIMENTS

Doped and undoped GeTe thin films were deposited by magnetron sputtering on 200 mm Si substrates. N-doped samples were prepared by reactive sputtering of a GeTe target using an Ar/N₂ gas mixture. C-doped samples were prepared by co-sputtering of GeTe and C targets. The compositions of samples were varied by changing the Ar/N₂ ratio for the N-doped samples and by changing the sputtering powers applied to the GeTe and C targets for the C-doped GeTe. The composition of the thin films were confirmed by Rutherford Back Scattering (RBS) for the Ge and Te compositions and by Nuclear Reaction Analysis experiment for C and N dopant concentrations. The thicknesses of the deposited layers and the deposition homogeneity are controlled by X-Ray Reflectivity (XRR) on the 200 mm samples.

Fourier-Transform InfraRed (FTIR) spectroscopy is used to probe vibrational mode of bonds in the GeTe films. For the FTIR analysis of our phase change thin film samples, 150 nm thick amorphous layers of C and N-doped GeTe were deposited on Si (100) wafers. Four different C and N dopant concentrations of 5, 10, 15 and 20 at % with an accuracy of ± 1 at % were deposited. A pure GeTe thin layer has also been deposited as non-doped reference sample. FTIR spectra of the samples were collected in transmission mode using BIORAD QS500 and Bruker VERTEX 80V FTIR spectrometers in order to cover the range from 100 to 4000 cm⁻¹. Prior to deposition the absorbance spectra of the silicon wafers have been acquired in order to remove the contribution to the absorbance spectrum of Si substrates due to Si phonons modes or for example dissolved element like O in silicon wafers. All spectra were recorded with a resolution of 2 cm⁻¹ and averaged over 64 scans for the 400-4000 cm⁻¹ range (High Frequency), and at 4 cm⁻¹ on 32 scans for the 100 to 400 cm⁻¹ range (Low Frequency).

In order to go further in this analysis, *ab initio* molecular dynamics simulations were performed on a 210 atoms box corresponding to Ge₅₂Te₄₈ doped with 16 at. % C and 10 at % N. The initial positions of Ge and Te atoms were those found in a previous simulation of amorphous GeTe [6]. Then C or N atoms were introduced by randomly substituting Ge and Te atoms. To simulate the dynamics of the system, we used the density functional theory implemented in the VASP code as described in Ref. [7]. After equilibrating the system at 3000K for 3 ps, we thermalized the liquid at 1073K for 10 ps. We then annealed the system down to the final temperature of 300K with a 30 K/ps ramp. At 700 K, the density was adjusted to minimize the effective stress on the simulation box. The obtained refined atomic density (0.0343 atoms/Å³) is larger than that of pure GeTe (0.033 atoms/Å³). Note that these values are close to the measured ones. The amorphous structural data were finally gathered by averaging relevant quantities over a 10 ps trajectory at 300 K. Finally, by analyzing these first-principles molecular-dynamics simulations boxes shown in figure 1, we are able to study the mechanical properties of GeTe and C or N doped GeTe by plotting the different vibrational modes of bonds present in the amorphous structure of pure GeTe or GeTe doped with 16 at. % C and 10 at. % N.

3. RESULTS & DISCUSSION

From DOS simulations illustrated by the boxes shown in figure 1, the structure of a-GeTe revealed to be different with the introduction of C or N dopant. In particular for a-GeTeC we observed the presence of Ge-C and Te-C bonds. But in case of a-GeTeN only Ge-N bonds are present while no Te-N bonds could be observed. This result is in good agreement with experimental XPS experiments published in ref [8-9]. Moreover a-GeTeC exhibits C linear chains, sp² C and tetrahedral C. In case of a-GeTeN we have 2 N₂ molecules and a majority of planar NGe₃ but only a few tetrahedral NGe₄.

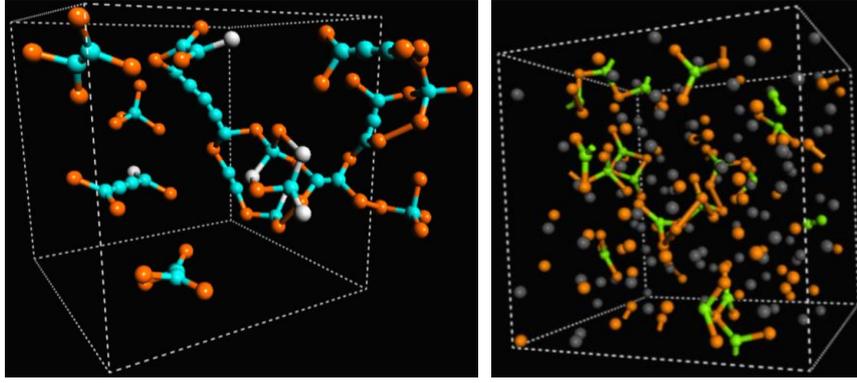


Figure 1: Instantaneous snapshot of a-GeTeC (left) and a-GeTeN (right) configuration at 300 K. Only C atoms (blue) or N atoms (green) and their first Ge (orange) and Te (white or dark grey) neighbors are plotted.

According to Maxwell rigidity theory and new constraint counting method [6] PCM are stressed rigid i.e. their internal degrees of freedom are limited by their high bond connectivity. This results in a number of mechanical constraint per atom $n_c > 3$ where $n_c = 3$ is the rigidity transition for which n_c is equal to the number of degrees of freedom in three dimensions. As a result in a-GeTe, a-GeTeN 10% and a-GeTeC 16%, we have $n_c = 4.7, 5.0$ and 5.2 constraints, respectively, to be compared for example to a-Ge₂Sb₂Te₅ for which $n_c = 3.6$.

In order to probe the impact of dopant on the amorphous phase stability we studied the effect of C and N dopants concentration on the vibrational properties of bonds in a-GeTe. Figure 2 (a) and (b) respectively show the FTIR absorbance spectra in the HF range from 400 to 2000 cm^{-1} of as-deposited C and N-doped a-GeTe with dopant concentrations varying from 0 to 20 at. %. In Figure 2 (c) and (d) are plotted the DOS of simulated vibrational modes of GeTe, GeTeC 16% and GeTeN 10%.

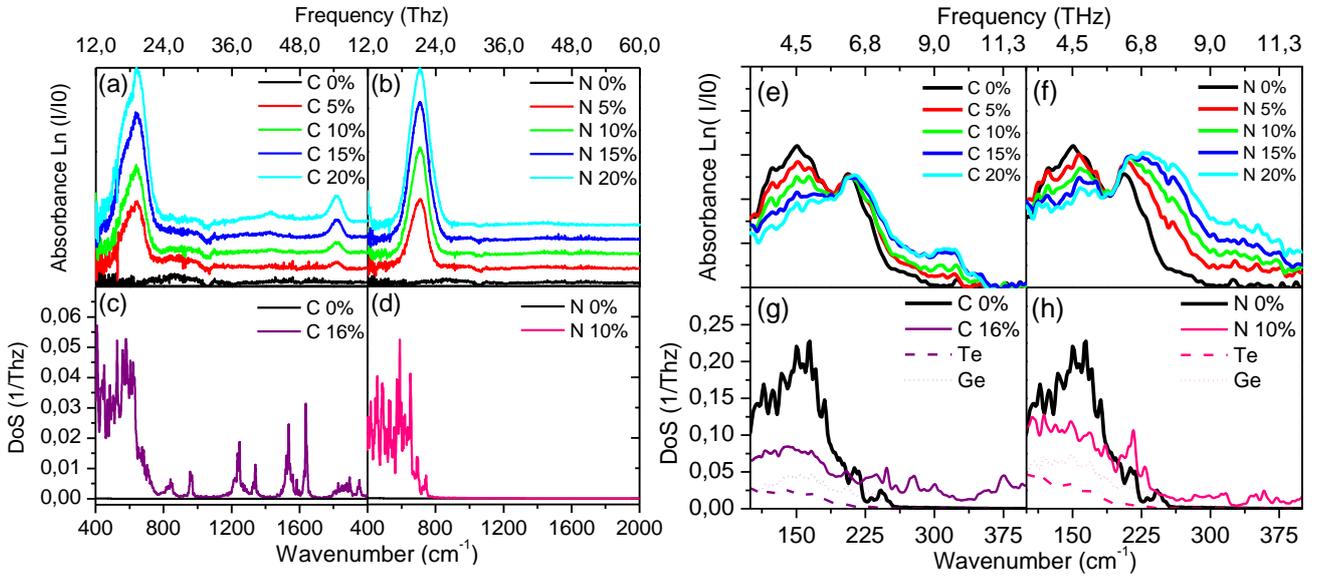


Figure 2: Experimental HF FTIR absorbance spectra of as-deposited a-GeTeC (a) and a-GeTeN (b) thin films and DOS simulations of vibrational modes of GeTe and GeTe doped with (c) 16 at.% of C and (d) 10 at.% of N.

LF FTIR absorbance spectra of as-deposited a-GeTeC (e) and a-GeTeN (f) thin films and DOS simulations of vibrational modes of GeTe and GeTe doped with (g) 16 at.% of C and (h) 10 at.% of N.

As shown by the dynamical properties studied by FTIR in figure 2 the transition from a-GeTe to doped a-GeTe is accompanied by the appearance of high frequency vibrational modes in the range 400 to 2000 cm^{-1} . In particular, at frequencies higher than 800 cm^{-1} , a large number of modes is present in case of C but not for N doping. We note that

the experimental spectra in figure (a) and (b) are in very good agreement with DOS simulations of vibrational modes presented in (c) and (d) for C and N doping. The origin of the vibrational modes measured between 800 and 2000 cm^{-1} in case of C doping is well explained by simulations. These modes are attributed to the C-C- stretching modes in a variety of different local environments. The large band appearing under 800 cm^{-1} for C as well as N doping can be attributed to the contribution of vibrational modes of C-Ge and C-Te bonds in tetrahedral CGe_4 for C doping, and to N-Ge modes in NGe_3 and to a lesser extent in NGe_4 for a-GeTeN. In the simulations, the differences of intensities and the dispersion of distinct modes across the whole frequency range have to be considered taking into account that the relatively small number of atoms inside the box that is effectively limiting the statistics. The more precise description of each vibrational mode contribution will be published elsewhere.

Figure 2 (e) and (f) show the LF experimental FTIR spectra obtained for C and N-doped a-GeTe. In figure 2 (e) and (f) two main vibrational bands are present on FTIR spectra of a-GeTeC and a-GeTeN. As shown by simulations in figure 2 (g) and (h) the first main vibrational band near 150 cm^{-1} present in a-GeTe decreases when C or N dopant is introduced in a-GeTe. This decrease is confirmed by experimental FTIR spectra of figure 2 (e) and (f) for which a more pronounced decrease is observed in case of C doping. Similarly, a strong decrease upon doping is also observed (not shown here) at lower frequencies, inaccessible to the experiment, but within reach of the AIMD simulations. These changes occur below 60 cm^{-1} , in the same wavelength range as that of the boson peaks generally observed in glasses. The decrease of this peak with doping shows the effect of doping on the stability of the amorphous phase of GeTe. Indeed this low frequency peak decreases as the dopant concentration increases with a more important effect for C compared to N. As previously shown for glasses the decrease of this boson peak can be correlated to the increase of the glass amorphous phase stability. By analogy, this correlates well with the increase of the crystallization temperature of a-GeTe when C or N dopants are introduced [1-3, 8]. The second band after 225 cm^{-1} in the LF absorbance spectra of C and N doped a-GeTe are due to vibrational modes induced by dopants. In particular it could be assigned for C dopant to bending and libration modes of C in C-C-C chains. In case of N doping the band after 225 cm^{-1} is well explained by simulations and is attributed to N-Ge modes in NGe_3 .

4. CONCLUSION

As it has been shown the introduction of carbon or nitrogen in GeTe strongly modifies its properties. This result is particularly interesting for applications in PCRAM technology for embedded applications in order to overcome the problems of data retention or current reduction. The introduction of C or N dopants in a-GeTe helps to increase its crystallization temperature T_x that is beneficial for the retention time. But the origin of this phenomenon remains unclear. In this paper, we have investigated the effect of dopant on the local structure of the amorphous phase of C and N-doped GeTe and the stabilizing effect of C and N doping on a-GeTe phase by vibrational modes analysis by FTIR and *ab initio* simulations. As a result we show that C and N strongly modify the amorphous structure of GeTe. Moreover, we have shown that the incorporation of C or N dopants drastically affects the mechanical properties of a-GeTe. The incorporation of N or C in a-GeTe induces two main effects: a depletion of modes at low frequency, similar to those of the boson peak commonly observed in other glasses, and an increase of high frequency localized modes due to doping elements. The modification of the vibrational modes goes with an increased number of mechanical constraints leading altogether to a more stressed rigid structure with a more pronounced effect for C than N giving a good explanation to the stabilization of a-GeTe by doping.

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