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Annealing influence on the magnetostructural transition in Gd5Si1.3Ge2.7 thin films

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Abstract
Due to the emerging cooling possibilities at the micro and nanoscale, such as the fast heat exchange rate, the effort to synthesize and optimize the magnetocaloric materials at these scales is rapidly growing. Here, we report the effect of different thermal treatments on Gd5Si1.3Ge2.7 thin film in order to evaluate the correlation between the crystal structure, magnetic phase transition and magnetocaloric effect. For annealing temperatures higher than 773 K, the samples showed a typical paramagnetic behavior. On the other hand, annealing below 773 K promoted the suppression of the magnetostructural transition at 190 K, while the magnetic transition around 249 K is not affected. This magnetostructural transition extinction imparts reflected in the magnetocaloric behavior and resulted in a drastic decrease in the entropy change peak value. Nevertheless, an increase in 25% of the TC and an increasing ΔTFWHM from 23 to 49 K of its operation temperature interval, ΔT, upon annealing, are crucial for future application in magnetic refrigeration.

Keywords
Magnetocaloric effect, Thin Films, Thermal treatment

Disciplines
Electrical and Computer Engineering | Electromagnetics and Photonics | Nanoscience and Nanotechnology

Comments
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Influence of Annealing on the Magnetostructural Transition in $Gd_5Si_{1.3}Ge_{2.7}$ Thin Film

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Due to the emerging cooling possibilities at the micro and nanoscale, such as the fast heat exchange rate, the effort to synthesize and optimize the magnetocaloric materials at these scales is rapidly growing. Here, we report the effect of different thermal treatments on $Gd_5Si_{1.3}Ge_{2.7}$ thin film in order to evaluate the correlation between the crystal structure, magnetic phase transition and magnetocaloric effect. For annealing temperatures higher than 500ºC, the samples showed a typical paramagnetic behavior. On the other hand, thermal treatments below 500ºC promoted the suppression of the magnetostructural transition at 190 K, while the magnetic transition around 249 K is not effected. This magnetostructural transition extinction was reflected in the magnetocaloric behavior and resulted in a drastic decrease in the entropy change peak value (of about 68%). Nevertheless, an increase in T_C was reported, proving that at the nanoscale, heat treatments may be a useful tool to optimize the magnetocaloric properties in Gd5(SixGe1-x)4 thin films.

Keywords: Magnetocaloric thin films, Thermal Treatment, Magnetocaloric effect,

I. INTRODUCTION

The recent success in the production of $Gd_5(Si_XGe_{1-x})_4$ thin films using femtosecond pulsed laser deposition opened new prospects for the optimization of the production process, with the aim of increasing the giant magnetocaloric effect (GMCE) in these nanomaterials [1,2]. It is well known that thin film properties are very

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sensitive to thickness, substrate type, oxygen content, as well as deposition and annealing parameters etc. [3]. For bulk materials, thermal treatments have been reported in the literature as a very important tool for both the minimization of secondary phases and optimization of the crystallographic phases responsible for the GMCE [4–8]. In fact, annealing temperatures below 700 K lead to an increase of the orthorhombic I, O(I), phase hence minimizing the MCE in $Gd_5Si_2Ge_2$ [4,6]. This is, in contrast to high temperature annealing, T=1473 K, where the phase transformation was from the lower volume, O(I), to the higher volume phase, Monoclinic, M, and shown an increase in the MCE [7].

However, for thin films, i.e. when the dimensions of a material are reduced, their phase diagrams suffer dramatic changes due to the different diffusion processes. In particular, the phase stabilization temperatures tend to be significantly smaller, meaning that less energy is necessary to activate the atomic diffusion at the micro/nanoscale. Hence, in order to unveil the effects of thermal treatments in the still unexplored $Gd_5Si_{1.3}Ge_{2.7}$ thin film, we studied the influence of annealing temperatures on the formation/destruction of the different crystallographic phases and their influence on morphology, structure and magnetic properties.

II. EXPERIMENTAL DETAILS

The preparation details of $Gd_5Si_{1.3}Ge_{2.7}$ thin films (~780 ± 25 nm thick) on SiO_2-covered Si substrates using femtosecond pulsed laser deposition and single crystal target were described in Ref [2]. In order to study the effects of different annealing temperatures, the samples were wrapped in a tantalum sheet, placed into a crucible, and introduced in a quartz tube with a zirconium getter to prevent oxidation. Four different temperatures were chosen for the presented study: 300, 400, 500, and 600ºC, with a fixed annealing time of 2 hours in vacuum (~10^{-5} mbar). The samples were fast cooled by immersing the sealed quartz tube in water, in order to quench the crystal structure. The morphological and structural characterization of the thin films was ensured by Scanning Electron Microscopy (SEM) and grazing incidence X-ray Diffraction (XRD). The magnetic measurements were performed in a commercial (MPMS Quantum Design) Superconducting Quantum Interference Device (SQUID) magnetometer. The magnetic entropy change [$-\Delta S_m(T)$] was estimated from the measured magnetic isotherms [M(H)] following the loop method [9].

III. RESULTS AND DISCUSSION

Figure 1a) shows the temperature dependence of magnetization for the $Gd_5Si_{1.3}Ge_{2.7}$ as-deposited film. On heating (red curve) it is observed that a first-order phase transition (FOPT) occurs from an orthorhombic O(I) ferromagnetic to an orthorhombic O(II) paramagnetic phase at T~194 K. However, this transition is incomplete and approximately 33% of the O(I) phase does not transform into O(II), meaning that at T>194 K the film consists of: two thirds [O(II), PM] and one third [O(I), FM] phase, as reported in [2]. At T~247 K, a purely magnetic second-order phase transition (SOPT) of the remaining [O(I), FM] phase occurs, changing its magnetic state from the ferromagnetic to the paramagnetic state (at T > 247 K) .

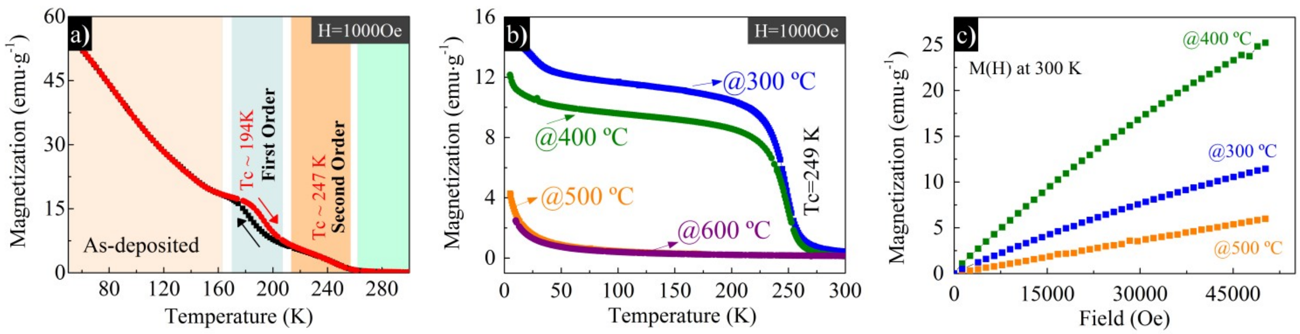

Figure 1 – (color online) The temperature dependence of the magnetization for the as-deposited sample measured at H=1000 Oe; b) Temperature dependence of the magnetization, measured at H=1000 Oe, for the samples annealed at: 300, 400, 500 and 600ºC; and c) Magnetization as a function of the magnetic field for the same annealing temperatures, measured at 300 K.

The effect of the annealing temperature is shown in Figure 1b). In fact, upon annealing at 300ºC and 400ºC, the films just present the SOPT at 249 K, previously observed in as-deposited film. Additionally, these annealing temperatures led to the disappearance of the FOPT.

If the annealing temperature is further increased, i.e., above 500ºC (Figure 1b), the two magnetic transitions observed in the as-deposited film disappear, and the film exhibit a pure paramagnetic behavior. Figure 1c) represents the M(H) curves measured at 300 K in the samples with different thermal treatments. The magnetic moment is higher in the sample annealed at 400ºC.

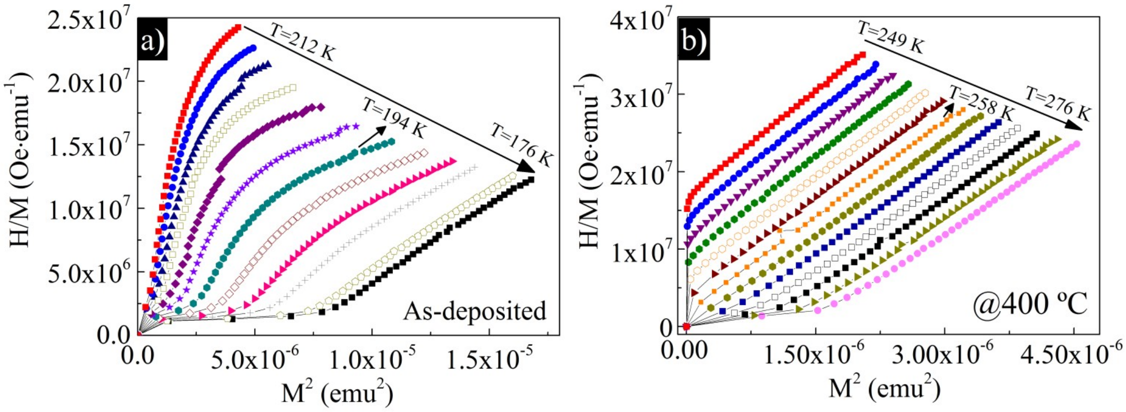

Figure 2 – (color online) Arrott plots, H/M as a function of M^2 for a) $Gd_5Si_{1.3}Ge_{2.7}$ as-deposited film measured in the temperature range [176; 212]K and b) sample annealed at 400ºC measured in [249; 276]K temperature range.

For the assessment of the nature of the thin film phase transitions and in order to confirm the disappearance of the MST-FOPT with the thermal treatments, the Arrott plots of the as-deposited sample and sample annealed at 400ºC were represented in Figure 2a) and b), respectively. For the as-deposited sample, the H/M vs M^2 exhibits a different behavior, changing from a negative to a positive slope with the increase of M^2 resembling an "S" shape. Such behavior is the signature of a first-order phase transition [10,11] and the confirmation that it occurs at Tc~ 194 K. On the contrary, the H/M vs M^2 curve of the film annealed at 400ºC shows a monotonous positive slope. Hence, this confirms the second order nature of the magnetic transition at ~ 247 K in the annealed film.

The XRD patterns extracted at 300 K are shown in Figure 3a). The as-deposited sample presents peaks corresponding to both the O(I) phase (Gd_5Si_4) and the O(II) phase (Gd_5Ge_4). After the thermal treatments, there is evidence of the decrease and vanishing of the peaks corresponding to the O(II) phase, such as the reflections: [0 4 0] (24.1º), [2 1 1] (26.5º) and [1 6 4] (61.8º) [12]. Concomitantly, there is an increase in the number of peaks corresponding to the O(I) phase, such as reflections: [2 2 1] (29.1º), [1 3 2] (31.7º) and [1 4 3] (44.5º) [13]. These results confirm the disappearance of the FOPT observed in Figure 1b), which is a direct consequence of the decrease in O(II) phase. The 33.2º and 47.4º peaks appear only after the thermal treatments and there is no correspondence to the O(I)/O(II) phases. Indeed, these peaks correspond to the Gd_2O_3 [14] phase, which may have formed because of the higher reactivity between Gd and O, but in low amounts due to the presence of Tantalum and Zirconium getters during annealing process. Many examples of phase transformations induced by annealing process on bulk $Gd_5Si_2Ge_2$ alloys can be found in the literature [5–7]. In these, several phenomena are responsible for the phase transformation such as, diffusion of Si, due to higher Si content, which may favor the O(I) phase [15] and stress release by the heating process [4].

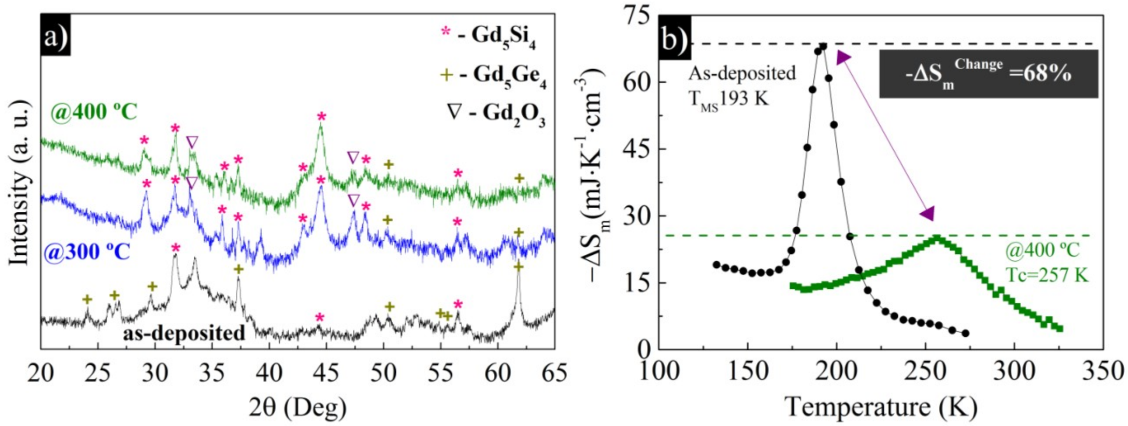

Figure 3 – (Color online) a) XRD pattern of the as-deposited film and films annealed at 300°C, and 400°C. The peaks are marked with symbols corresponding to different crystallographic phases; b) Temperature dependence of the $-\Delta S_m$ of the as-deposited film and the films annealed at 400°C under an applied magnetic field change of 50 kOe.

Figure 3b) shows the $-\Delta S_m$ of the as-deposited and annealed (at 400ºC) films. The maximum magnetic entropy change, $-\Delta S_m^{max}$, is 68 $mJK^{-1}cm^{-3}$ for the as-deposited at around 193 K. After the thermal treatment, there is a 68% decrease of the $-\Delta S_m^{max}$ value to25 $mJK^{-1}cm^{-3}$ and occurs at T ~ 257 K. This decrease results from the destruction of the [O(II), PM] $\rightleftharpoons$ [O(I), FM] MST that occurs in the as-deposited film at T ~ 193 K. Moreover, the temperature at which $-\Delta S_m$ is maximum was found to increase by 25%, i. e., from 193 K to 257 K.

As previously reported, materials presenting coupled magnetic and structural transitions exhibit a much higher MCE because of the extremely large dM/dT value at the transition (which is a critical parameter for the enhancement of the magnetic entropy change) and also because there is an extra entropy change associated with the lattice transformation, $-\Delta S^{lattice}$ [16]. Therefore the reduction of the $-\Delta S_m^{max}$ value with annealing temperature was expected since the MST was suppressed. Previously, in $Gd_5Si_2Ge_2$ bulk material, Pecharsky and co-workers [5,17] found a $-\Delta S_m$ decrease and a T_C increase in samples annealed at 670 and 870 K and attributed such reduction to the formation of the O(I) phase with the annealing. The Full Width at Half Maximum (FWHM) was estimated from the

$-\Delta S_m$ curves and an increase with the annealing process was observed, from 23 to 49 K. The larger FWHM is a signature of a SOPT and in this film, it might also be associated to strain disorder [18]. The refrigerant capacity value ($RC = -\Delta S_m^{max}$ x FWHM) was estimated to be ~203 JKg^{-1} and ~160 Jkg^{-1} for the as deposited and 400º C annealed film, respectively, with a ΔH=5T field variation. Hence, despite the large 68% decrease on the $-\Delta S_m^{max}$, the thermal treated film shows only a small decrease on its RC (21%) because of its larger FWHM. Simultaneously, a larger FWHM represents an expanded interval of operational temperatures (and closer to room temperature) of a potential magnetic refrigerator/sensor.

IV. CONCLUSIONS

In this work it was found that thermal treatments below 500ºC were responsible for the suppression of the MST in $Gd_5Si_{1.3}Ge_{2.7}$ thin films. This was confirmed by the disappearance of the O(II) phase in the XRD measurements. The suppression of the structural phase responsible for the GMCE promoted a 68% decrease in the magnetic entropy change peak value and a 21% decrease in its RC. Nonetheless, there was a 25% increase in T_C, which is closer to room temperature, and a ~ 110% expansion of its operational temperature interval upon annealing. These findings are crucial for future application in magnetic refrigerators/sensor. Hence this work demonstrates that thermal treatments of thin films can be an important tool to promote and optimize the crystallographic phase responsible for the GMCE.

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