Magnetocaloric Gadolinium thick films for energy harvesting applications

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Magnetization, Curie temperature and isothermal entropy change have been measured in Gadolinium 3 μm thick films. We present the comparison between the structural and magnetic properties of samples deposited either at room temperature or at 550°C onto silicon substrate (100) with a thermally oxidized layer. The results are discussed using as a reference, data from bulk Gd single crystals. As compared to bulk values, the room temperature grown film shows lower Curie temperature ($\sim$ 280 K) and weaker entropy change ($\sim$ 6.8 Jkg^{-1}K^{-1}) under application of magnetic field ramp from 0 to 5 Tesla. On the contrary the 550°C deposited film shows a Curie temperature ($\sim$ 293 K) and a maximum isothermal entropy change ($\sim$ 8.9 Jkg^{-1}K^{-1}) both in good agreement with values expected for bulk samples. The behavior of the room temperature deposited samples are briefly discussed and compared with similar effects observed in bulk samples with different degree of purity and homogeneity.

I. INTRODUCTION

Improving energy efficiency and cutting greenhouse emissions have been the main motivation of the last two decades intense research activity in the field of caloric materials[1]. The research of new solid state cooling devices has been focused on bulk magnetocalorics (MC) with a particular emphasis on efficiency[2]. Recently a growing interest in energy harvesting applications with some emphasis on the micro and nano scales has triggered a paradigm shift towards the research of higher power output[3,4]. Gadolinium has been the benchmark material for bulk cooling devices and its study will be extremely relevant as well for development of micro-scale harvesting devices where the comparison between first and second order MC performance is still an open issue[5]. Despite the great interest for application, the use and characterization of Gd films are still rather preliminary with some controversial results concerning the substrate role in modifying magnetic moment, and Curie temperature[6]. High throughput thermogeneration at the micro-scale requires relatively thick films and a reduced thermal influence from the substrate. Therefore a detailed characterization of magnetic and MC properties on thick Gd film as a function of thickness and of the growth conditions is in order. Here we study Gd thick films deposited either at room temperature (RT) or at 550°C using a sputtering machine (below we shall refer to them as the RT and the 550°C sample). Magnetic properties including magnetization as a function of temperature, magnetic field, and entropy change are investigated using a SQUID and a VSM-PPMS. Crystal structure has been characterized using a high precision XRD machine. Our results show the influence of growth temperature on crystal structure. Notably we observe high temperature growth sharpens the transition, and slightly shifts Curie point toward higher temperature increasing the maximum entropy change.

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The main issue we would like to address in this work is the relative lack of systematic studies on Gd films in a thickness range between few and tens of microns. A decrease in saturation magnetization and entropy change, with respect to bulk reference values[7], has been observed for thin films with thicknesses in the nm range[8–11].

II. RESULTS AND DISCUSSION

Gd 3 μm thick polycrystalline films were grown on Si (100) single crystal substrate (275 μm thick) with a thermally oxidized layer of 290 nm SiO_2 by a DC sputtering system. Deposition has been done in Ar atmosphere under a base pressure of 1×10^{-7} mbar and a depositing pressure of 1×10^{-2} mbar. A 85 mm diameter Gd target with a high purity of 99.9% has been used. Distance between sample holder and target is 65 mm. Tungsten was used as a buffer and as capping layer. Gd thick films were deposited at room temperature (RT) and at 550°C with a sputtering power of 100 W. The growth rate and film thickness were estimated using a scanning electron microscope (FESEM). The error on the thickness evaluation is estimated at about 5% because of the sample roughness and of experimental uncertainty.

Structural characterizations of Gd thick films have been carried out using high resolution $\theta-2\theta$ scans (see the left hand side image in Fig 1). After deposition, the fractured cross-sections of the samples have been measured to estimate film thickness. All the samples studied here show the following structure: Si(100)/SiO_2// W/Gd 3 μm/W. A thin 15 nm W capping layer has been used to protect Gd from oxidation. The in-lens image measured by FESEM shows a continuous film without cracks or intermixing between sample and substrate (see the right hand side image in Fig 1). No appreciable structure differences are observed between the RT and the 550°C deposited film.

According to Rietveld refinement, the XRD data yield lattice parameters a = 3.6595(8) Å, c = 5.85(7) Å for the RT deposited film and a = 3.636(4) Å, c = 5.79(07) Å for the 550°C one. XRD diffractograms from both samples (see the left hand side image in Fig 1) show the expected hcp Gd struc-

ture without traces of oxidised or fcc Gd phases. In particular, no Gd_2O_3 peak has been detected[12,13]. Polycrystalline films show different preferential c axis orientation as apparent from the diffractograms shown in the left hand side image of the Fig 1. More detailed investigations will be presented elsewhere.

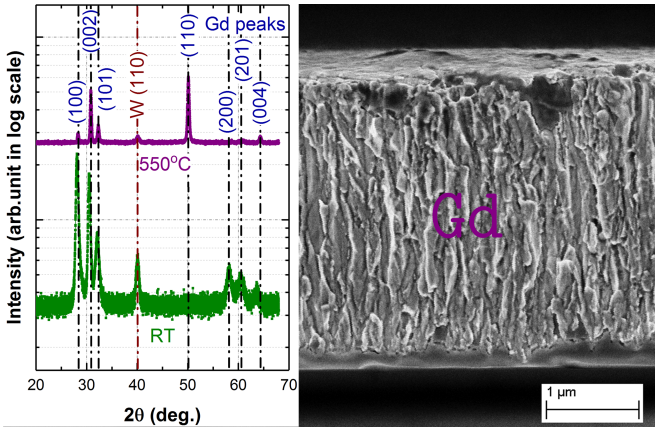

FIG. 1: The XRD results in log scale and a topographical image of Gd thick film deposited at 550°C are shown on the left and right hand side, respectively. In the XRD figure at the left hand side, the olive and purple curves are the RT and 550°C films, respectively.

Compared with the bulk hcp structure[14], the RT deposited sample shows a slight increase in volume ($\sim 2.4\%$), while the 550°C sample is in good agreement with the reported bulk values. While the maximum intensity reflection of the 550°C deposited film is (110), the maximum reflection of the RT one is (100) (the purple/top and olive/bottom curves respectively, shown on the XRD image in Fig 1).

Magnetization measurements as a function of temperature M(T) were performed using a Quantum Design MPMS XL. The measurement is carried out on 2.5×2.5 mm^2 samples with the applied magnetic field parallel to the film surface. The estimated error on the reported magnetization is about 5% mainly due to the thickness evaluation uncertainty. The thermo-magnetic curves M(T) measured under different fixed fields ($H = 0.05, 1, 5$ T), on the Gd films deposited at RT (olive points) and 550°C (purple points) are shown in Fig 2 (the left hand side image). Maximum magnetization at 10 K under a 0.05 T applied field is about 741 and 1153 kA/m for films deposited at RT and 550°C, respectively. We can see that the magnetization of the film deposited at 550°C is higher than the one deposited at RT whatever the external field intensity is.

Under 5 T the magnetization curves of the two films get closer, e.g. $\sim$ 2041 and 2219 kA/m at 10 K for the RT and 550°C sample, respectively with an estimated uncertainty of about 5% mainly due to the thickness evaluation. Measurements at 5 T also show a better agreement with the bulk values. As expected in the case of a second order phase transition, no thermal hysteresis has been observed during heating and cooling process.

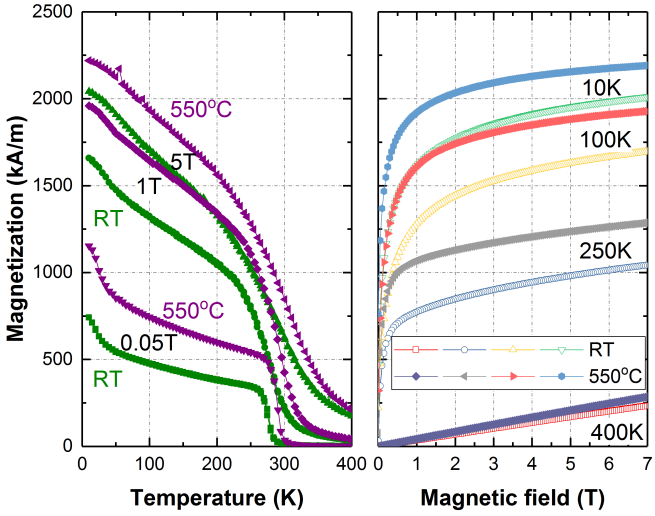

FIG. 2: M(T) curves under magnetic fields: 0.05 T, 1 T, 5 T for Gd thick films deposited at RT and at 550°C in the left hand side. The right hand side figure is a comparison of isothermal magnetization curves measured at 10K, 100K, 250K and 400 K on RT (empty symbol) and 550°C (full symbols) deposited samples.

The magnetization anomaly observed in low applied field thermomangetic curves at $T_{SR} = 25$ K in both samples has been reported in the literature and have been be attributed to the interplay between texturing and a spin reorientation transition[8,10,15].

The study of this anomaly is beyond the scope of this article. Here we focus on the magnetic properties near the phase transition temperature where the magnetocaloric effect is relevant. Moreover high temperature deposition leads also to an increase in the Curie temperature and a sharpening of the curve near the ferromagnetic-paramagnetic transition.

Isothermal magnetization curves were measured on both films from 400 K to 10 K in order to estimate the Curie temperature (T_C) and entropy change, using a Quantum Design vibrating sample magnetometer. Measured isotherms at low ($T = 10, 100, 250$ K) and at high ($T = 400$ K) temperature are shown in the Fig. 2 (the right hand side image). In both samples the paramagnetic behavior is apparent for higher temperature isotherms. Isothermal $M(H)$ measurements present similar shape and slope (i.e. same apparent permeability) showing that the measured difference can hardly be explained invoking a residual anisotropy in the RT sample.

The Curie temperature of the two samples has been determined (i) by extrapolation the M(T) curve from the inflection point and then taking the intercept with the x-axis[16], (ii) from isothermal magnetization measurements, through the Arrott plot method, and (iii) from the isothermal entropy change maximum ($-\Delta S_{max}$) using Maxwell relations on the measured isotherms.

The Curie temperatures of the RT and 550°C films using the first method are 285 K and 297 K respectively, under an applied magnetic field of 0.05 T. The Arrott plot extrapolated Curie temperatures are 281.7 K, and 298 K for the RT and

for the 550°C sample, respectively. The Curie temperatures of the RT film in both two methods are definitively lower than the reference bulk $T_C = 294$ K from Belov et al[17] or $T_C = 295$ K from Lyubina et al[14]; the T_C of the 550°C film, considering the applied magnetic field in the first method and the lack of linearity of the $M^2(H/M)$ curves in the Arrott plot, is very possibly slightly overestimated but still within the error interval with the aforementioned bulk value.

Beside Curie temperature, isothermal entropy change ΔS is a key parameter in order to characterize the MC effect. Here, we extrapolate the magnetic entropy change from the isothermal magnetization curves using Maxwell relation: $\Delta S = \mu_0 \int_0^{H_f} \left(\frac{\partial M}{\partial T}\right)_H dH$. Entropy changes as a function of temperature, under field changes in the $0 - H_f$ interval (with $H_f = 1,3,5,7$ T), estimated using using Gd bulk mass density of 7.9 g/cm^3, are shown on figure 3. Determination of the maximum entropy change as a function of temperature is used as an alternative method to extrapolate the Curie point. Moreover, it is of practical interest for magnetocaloric applications. Both samples show $-\Delta S(T)$ maxima in agreement with the Arrott plot determined critical temperatures. Consequently, it is worth to be reported that the obtained ΔS results are affected by uncertainties (+/- 5%) due to the aforementioned magnetization density evaluation.

For the RT deposited film the maximum entropy change is measured at 280 K and is $(-\Delta S_{max}) = 6.8$ Jkg^{-1}K^{-1} for a magnetic field ramp from 0 to 5 Tesla, and $(-\Delta S_{max}) = 8.7$ Jkg^{-1}K^{-1} for a magnetic field change from 0 to 7 Tesla. These values are higher than the ones reported in literature for Gd thin films[9], but are smaller than bulk values from Dan'kov et al.[7] where $(-\Delta S_{max}) = 10.3 \pm 1.7$ Jkg^{-1}K^{-1}. It is worth noting that the mass density of RT samples is lower than the bulk one resulting in a slight under estimate of ΔS values.

For film deposited at 550°C temperature dependence of entropy change shows a peak at 293 K, in agreement with the Curie temperature of the bulk Gd, and whereby confirming that for this sample the Arrott plot gives a quite overestimated T_C value. The entropy change at 293 K is around 8.9 Jkg^{-1}K^{-1} and 11.2 Jkg^{-1}K^{-1} for a magnetic field of $0-5$ T and $0-7$ T, respectively. Slopes are also sharper than the ones in sample deposited at RT.

The difference in shape of the $\Delta S(T)$ curves between the two samples, as well as the T_C and $(-\Delta S_{max})$ lowering observed in the broader curve (i.e. the one corresponding to the RT deposited film) can be interpreted as due to the influence of impurities making the RT sample less homogeneous. Indeed it has been shown[14] that defects, particularly purity and crystallization, induce a distribution of T_C of width ΔT_C, reduce the isothermal entropy maximum following the expression $(-\Delta S_{max}) = AH^{2/3} - B\Delta T_C$, where $A = \alpha/(4b)^{2/3}$ and $B = \alpha^2 \Delta T_C/18b$ are material intrinsic parameters related to the Landau expansion coefficients α and b. Moreover the temperature corresponding to the entropy maximum is expected to be reduced following $T_{max} = T_C - \gamma \Delta T_C$, where γ is a coefficient dependent on the shape of the T_C distribution. This approach permits a comparison to evaluate our thick films with bulk Gd values.

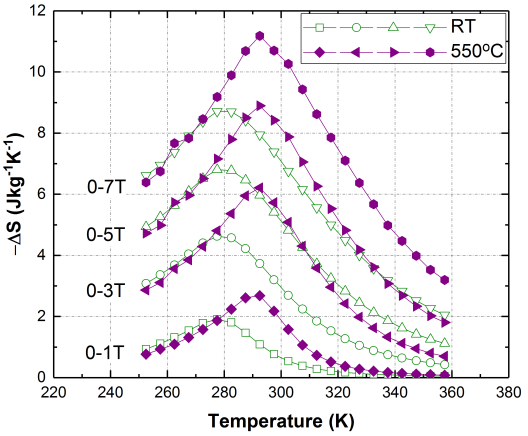

FIG. 3: Entropy change of samples deposited at RT and 550°C

Using the relation between ΔS_{max} and $H^{2/3}$ above together with the left slope of $\Delta S_{max}(T)$ peak, $\alpha/6b$, we estimated $\Delta T_C \sim 12.8$ K for the 550°C deposited film which is consistent with published data for polycrystalline Gd bulk[14]. Assuming that the shape of the distribution is rectangular and $\gamma = 1/6$ [18], the Curie temperature is estimated $T_C \sim 295$ K for the 550°C sample with $T_{max} \sim 293$ K. A similar procedure yields $\Delta T_C \sim 24.4$ K and $T_C \sim 284$ K for the sample deposited at RT. The distribution width increase in ΔT_C suggests a higher contribution of impurity and inhomogeneity in the RT deposited sample than in the 550°C one.

About the mechanism underlying the broadening of T_C distribution in RT sample we can but put forward some preliminary hypothesis. Considering the film thickness, a mechanism just relying on interface coupling between film and substrate looks quite unlikely. Nevertheless we shall devote further studies on films with different thicknesses. On the other hand, growth temperature can affect film texturing and its coupling with local strain.

III. CONCLUSION

Our results show that films with 3 μm thickness can indeed achieve MC properties comparable to the one of bulk single crystal but that growth conditions, notably deposition temperature, must be wisely chosen. The 3 μm Gd film deposited at 550°C we present here shows a Curie temperature and an entropy change close to the reference bulk values, with $T_C \sim$ 293 K and $(-\Delta S_{max}) \sim 8.9$ Jkg^{-1}K^{-1} under the application of magnetic field change in the 0-5 T interval. Comparison with a similar sample deposited at lower temperature reveals the relevance of deposition temperature in order to optimize film properties. Moreover we show that the RT deposited properties can be ascribed to a local distribution of T_C possibly related to the interplay between texture and residual strains, or to the presence of Oxygen and Hydrogen inclusions.

This result is a first step towards our final goal to produce magnetocaloric films to be used as active substance in energy

conversion micro-devices working at high cycling frequency because of their excellent surface/volume ratio (viz. getting a faster thermal exchange at the thermal reservoirs). The prominent role of thickness reduction in order to improve caloric material based thermo-generation has been recently emphasised for pyroelectric materials[19]. The key point is that the main factor limiting cycling frequency is the time t heat needs to spread through the material, and $t \propto d^2$ where d is the material thickness. As the energy contribution E from the active material scales as volume we have $E \propto d$. Using a caloric thin film shall drastically reduce volume, nevertheless the maximum power output is $P_{max} = E/t$ so that $P_{max} \propto 1/d$ paving the way to high frequency/power output devices (e.g. a reduction of the active material from 500 μm to 5 μm makes possible a two orders of magnitude frequency improvement).

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