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Production of thick Gd freestanding films for energy conversion applications

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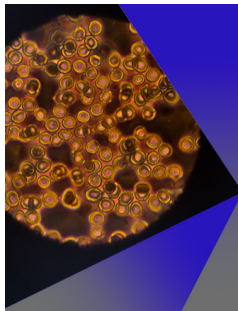


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ABSTRACT

The use of magnetocaloric material in microelectromechanical energy conversion devices requires freestanding films with smooth surfaces to allow fast and efficient heat transfer. We present and discuss a mechanical method to produce freestanding thick Gadolinium films showing excellent magnetic properties, and high-quality surfaces on both sides. Polycrystalline Gd films have been prepared by sputtering on a silicon substrate with a thermally oxidized layer with different thicknesses. Films have been grown at 543 K. Tantalum and Tungsten have been used as buffer layers because of their corrosion resistance and of their thermal conductivity. The magnetic and surface properties of the freestanding films are presented, with special focus on the role of using different capping layers. Full characterizations of the three freestanding Gd films, including AFM measured surface roughness, XRD patterns, Curie temperature, thermo-magnetic curves, and maximum entropy change, are presented and discussed.

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I. INTRODUCTION

Bulk Gadolinium (Gd), due to its near room temperature Curie point T_c , has been, for the last 25 years, the benchmark for application of magnetocaloric effect (MCE) to cooling devices using, as an active principle, a solid state substance.^{1,2} Recently, it has been pointed out that Gd films can play a similar role for the upcoming applications of MCE in the field of microelectromechanical systems (MEMS).³ In this framework, film aspect ratio represents a key issue to keep the material diffusivity high, making thermal exchange through the surface easier, and faster. Understandably, beside the need for good magnetic properties (i.e. saturation magnetization, Curie temperature, entropy change) similar to the one obtained in high purity bulk samples, films must be freestanding, not to hinder heat exchange and caloric effect, and must show smooth surfaces on both sides.

We recently discussed the role of growth-temperature in obtaining thick Gd films, on silicon substrate, with magnetic properties near to the bulk ones.⁴ Moreover, we recently presented 17 μm thick freestanding Gd films, focusing on their smooth surface, and on their flexibility after a mechanical peeling-off of the Silicon substrate.³

In what follows, we shall study the role of the capping layer choice, in obtaining wide (i.e. with size between 2 and 35 mm wide) freestanding films, with high-quality surfaces, and showing good magnetic properties. Deposition well above room temperature, as we put in Ref. 4, is a key issue to get optimal magnetic properties. In addition, this parameter strongly affects the residual stress distribution within the film, and at the interface between film and substrate, as well as the polycrystalline structure (i.e. defects, crystallite size). All these issues can modify the mechanical properties, making the

substrate removal difficult and reducing the final quality of the film surface.

Here, the surface quality and the magnetic properties of a series of Gd films deposited on Silicon are studied after the removal of the substrate. Samples with thickness ranging from $7\ \mu\text{m}$ to $17\ \mu\text{m}$ have been grown at 543 K using Tantalum (Ta) or Tungsten (W) as buffer and capping layers. The impact of buffer and capping layers on the resulting freestanding film properties is discussed.

II. EXPERIMENTS

Gadolinium films have been deposited on silicon (100) substrates with a thermally oxidized layer (SiO_2) by DC magnetron sputtering, in argon atmosphere. A 85 mm diameter, 99.9% purity Gd target has been used. While the base pressure was approximately 10^{-7} mbar, the deposition pressure was 10^{-2} mbar. Tantalum and Tungsten have been used as a buffer and capping layer. Thicknesses of the buffer and capping layer are 100 nm and 15 nm, respectively. Crystal structure, magnetic properties, cross-section images and surface morphology have been acquired by X-ray diffraction (XRD) - Rigaku SmartLab, VSM/SQUID - Quantum Design PPMS, MPMS XL, with a field emission scanning electron microscope (FESEM) - Zeiss SUPRA and by atomic force microscopy (AFM) - Park Systems NX20.

A. Mechanical substrate removal

Substrate removal has been carried out mechanically. After tracing a superficial groove on the silicon layer, using a diamond pen, the metallic side has been pushed against a slightly convex surface, as shown in Fig. 1, allowing to peel-off the silicon layer without damaging the Gd one.

As most of the rare-earth elements, Gadolinium is extremely reactive and easy to oxidize. Hence, the use of buffer and capping layers is necessary to avoid reaction with the silicon substrate and oxidation as well. As our goal is to obtain freestanding films

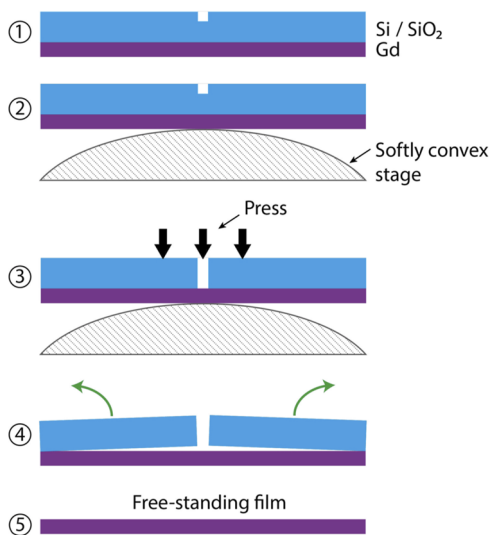


FIG. 1. Removing substrate to obtain freestanding films in 4 steps.

with smooth surfaces on both sides, comparing the way different buffer and capping elements can affect the substrate removal procedure, and the resulting surface quality represents a pretty relevant issue.

Here, we compare two buffer and capping substances, Tantalum and Tungsten, commonly used because of their resistance to corrosion, and of their good thermal conductivities.

It is worth noting that, growth temperature above 543 K, beside being necessary to get optimal magnetic properties, is beneficial also to be able to properly remove the substrate. Indeed, the above described mechanical substrate removal resulted in irreversible film damages when samples, of different thicknesses (i.e. 3, 7, $17\ \mu\text{m}$), prepared with both Ta and W buffer layers, have been deposited at temperatures below 543 K.

The first relevant difference between Ta and W buffer concerns the substrate removal, definitely easier on Ta-buffered films. In this case, freestanding films with large surfaces (i.e. up to $35 \times 35\ \text{mm}^2$) have been obtained without difficulties. On the contrary, most of the W-buffered films can be hardly completely detached from the silicon layer. More precisely: the 3 and $7\ \mu\text{m}$ films got irreversibly damaged during the substrate removal. A $7 \times 7\ \text{mm}^2$ freestanding film has been obtained from the $17\ \mu\text{m}$ one whose surface and magnetic properties are presented in the following sections. Only by increasing the growth temperature of the W-buffered $17\ \mu\text{m}$ thick film up to 666 K, it has been possible to obtain a freestanding film of larger area, up to $\sim 12 \times 12\ \text{mm}^2$. However, as we shall show below, this treatment showed a detrimental effect on the surface smoothness.

A possible explanation of the easier delamination of Ta with respect to W can be related to their different adhesive properties. The adhesive value depends on interfacial bond strength, hardness, elasticity or surface roughness. The scratch test is considered as the best semi-quantitative assessment method of adhesion,⁵ and, because of its higher hardness, W is expected to be more difficult to scratch than Ta. This leads to the easier delamination when using Ta. Moreover, while during cutting and breaking of the Si substrate we observed edge flaws when using Ta, we didn't observe them when using W, as apparent from the FESEM published in Ref. 4. Most of the mechanical energy required to peel the film is due to inelastic bending⁶ making the energy needed to delaminate Ta-buffered films smaller than the one needed to delaminate the W ones. As edge flaw is known for reducing significantly the energy needed during delamination,⁵ this can be an additional reason for the difference observed between Ta and W-buffered films.

B. Freestanding film microstructure

Freestanding films using both Tantalum and Tungsten as a buffer layer present a dense and continuous structure (see Fig. 2). A slight morphological difference can be appreciated as the W/Gd/W film shows a columnar structure, while the Ta/Gd/Ta film shows rounder grains and shorter columns.

X-ray diffraction (XRD) equipped with a copper X-ray source ($\lambda \sim 1.540593\ \text{\AA}$) has been carried out to characterize the film crystal structure. Due to the thickness, X-rays can not probe the whole film so that we performed XRD on both sides (see Ref. 3 for more details). We shall refer to the side formerly in contact with the substrate as the

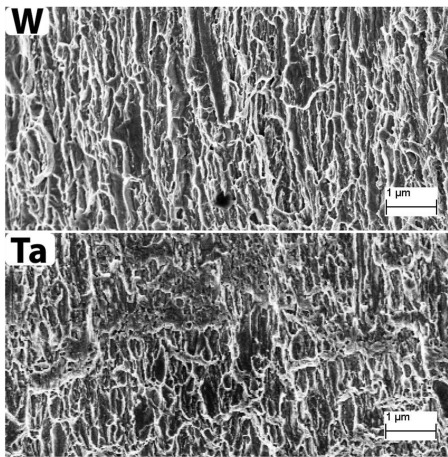


FIG. 2. In-lens cross-section FESEM image of the Gd film using Tungsten (top) and Tantalum (bottom) as buffer and capping layers.

bottom, and to the other as the top. Fig. 3 shows XRD spectra measured on top side of 17 μm thick Gd freestanding films buffered with Ta (top frame), and W (bottom frame). Both films show a hexagonal close packed structure with lattice parameter $a = 3.6335 \text{ \AA}$, a

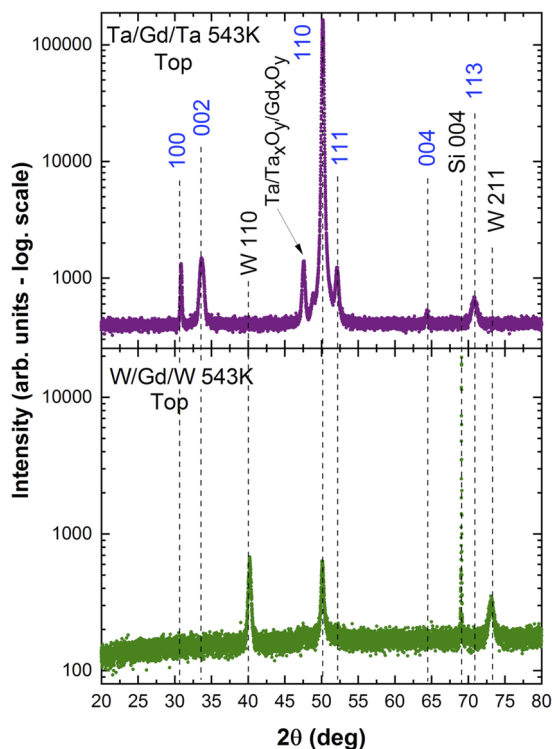


FIG. 3. XRD pattern of the Gd film using Tungsten (the image on bottom) and Tantalum (the top image) as buffer and capping layers. The thickness of both films is 17 μm .

value close to the one of bulk Gd, $a = 3.6336 \text{ \AA}$.⁷ The main reflection for both film is 110. Actually, when using Tungsten 110 is the only appreciable peak. On the contrary, for the film using Tantalum, beside the main reflection at 110 which is high and narrow, other peaks are apparent. The relative intensity of the secondary peaks is below 0.5%. The preferred orientation of the W/Gd/W sample is 110 on both film sides, while a difference between the top and bottom side (110 and 002, respectively) of the Ta-buffered film has been observed.³ Nonetheless, beyond slight differences, all the XRD patterns show the high-quality of both freestanding films.

C. Surface morphology

Getting smooth surfaces is one of the key objectives when aiming applications relying on heat transfer through direct contact.^{3,8} Freestanding films surfaces have been studied by AFM in order to determine their morphology and their roughness.

Surface morphology of the Ta and W films grown at 543 K (see figure 4 a-c) is rather similar, as apparent from Fig. 4, with the remarkable exception of the W-buffered film deposited at 666 K. The mean roughness (R_a) and the root mean squared roughness (R_{RMS}) keep in the 9 – 10 nm and 11 – 15 nm intervals, respectively (see Table I). The bottom roughness is slightly different due to the contact with substrate during the growth, $R_a \sim 1 - 3 \text{ nm}$ and $R_{RMS} \sim 2 - 4 \text{ nm}$ (see bracketed values in Table I). In addition, surfaces are mirror like on both sides. It is worth noting that deposition at higher temperature allows a further improvement of the magnetic properties,³ and makes substrate removal easier. However, it may reduce the surface quality as apparent from the dramatic roughness increasing observed in the W-buffered and 17 μm thick freestanding film reported in Table I (also see figure 4d). Indeed, above a deposition temperature of about 550 K, a tradeoff between magnetic properties and surface quality has to be taken into account.

D. Magnetic properties

Here, we compare magnetic properties of Ta-buffered 7 μm and 17 μm ³ thick freestanding films, and of a W-buffered 17 μm thick one. Actually, it has not been possible to remove a W-buffered 7 μm thick film from the substrate without damaging it. All the three samples studied in this section have been deposited at 543 K.

The main frame of Fig. 5 shows the thermomagnetic curves measured on the three samples under a 0.05 T applied field. The Ta and W-buffered 17 μm films show rather similar properties. On the contrary, the 7 μm Ta/Gd/Ta film better saturates under the application of a low field. Nonetheless, the three samples show the same T_c and their thermomagnetic measurements collapse onto the same curve under the application of a 5 T field, as shown in the inset of Fig. 5. Hence, the observed low field difference is expected to be related to the texturing and to some residual stresses modifying the behavior of thicker films. A more detailed study of the relationship between film thickness and magnetic properties will be presented elsewhere.

The overall error due to uncertainties in determination of sample volumes is estimated at $\sim 10\%$. The Curie temperature has been determined using the following methods:³ (i) from the vanishing magnetization point from $M(T)$ at a low magnetic field, (ii) from

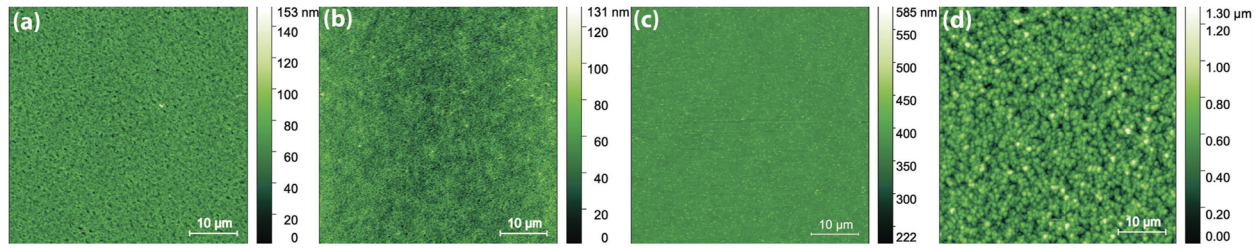


FIG. 4. AFM images of Gd films deposited at 543K: (a) Ta/Gd 7 $\mu\text{m}/\text{Ta}$, (b) Ta/Gd 17 $\mu\text{m}/\text{Ta}$, (c) W/Gd 17 $\mu\text{m}/\text{W}$, and (d) W/Gd 17 $\mu\text{m}/\text{W}$ deposited at 666 K.

the first derivative $\partial M/\partial T$ against T at low magnetic field, (iii) from the temperature at which specific heat gets maximum, (iv) from susceptibility measurements.

All these techniques confirmed a T_c within the 292 – 293 K interval, in agreement with previously published results,^{3,4} and with the values reported in the literature on bulk Gd.^{7,9}

TABLE I. Roughness of the top of Gadolinium films deposited at 543 K using Tantalum and Tungsten as buffer and capping layers. The value in brackets is the roughness of the bottom that has been in contact with the Silicon substrate before its removal. We added the W/Gd 17 $\mu\text{m}/\text{W}$ freestanding film deposited at 666 K for comparison.

Sample	R_a (nm)	R_{RMS} (nm)
7 μm - 543 K - Ta	9.2 (1-3)	11.7 (2-4)
17 μm - 543 K - Ta	10.3 (1.8)	12.8 (2.6)
17 μm - 543 K - W	10.8 (2.4)	15.1 (3.1)
17 μm - 666 K - W	121.6 (0.8)	152.3 (1.1)

A set of isothermal $M(H)$ curves measured from 360 K to 250 K has been used to work-out the entropy change using the Maxwell relation:²

$$\Delta S = \mu_0 \int_{H_i}^{H_f} \left(\frac{\partial M}{\partial T} \right)_H dH. \quad (1)$$

Using the density of bulk Gd, namely $7.910^3 \text{ kg m}^{-3}$, the maximum entropy changes are $(-\Delta S_{\text{max}}) = 4.6, 4.4 \text{ J kg}^{-1} \text{ K}^{-1}$ at $H_f = 2 \text{ T}$ for 7 and 17 μm freestanding films, respectively. The temperature where the entropy change reaches its maximum is approximately 293 K. We also plot the maximum entropy change following the power law expected from mean-field approach, namely $(-\Delta S_{\text{max}}) \propto H^{2/3}$ ¹⁰ shown in the inset of Fig. 6.

The maximum entropy shown in Fig. 6 by the Gd freestanding films presented here is higher than the one reported for thin films and ribbons,^{11,12} but it is still lower than the one reported for Gd single crystals,⁹ i.e. $(-\Delta S_{\text{max}}) \sim 5.5 \text{ J kg}^{-1} \text{ K}^{-1}$. Increasing growth temperature and post-annealing processes represents two possible ways to improve the magnetic properties.^{3,12} A detailed study on these techniques will be presented elsewhere.

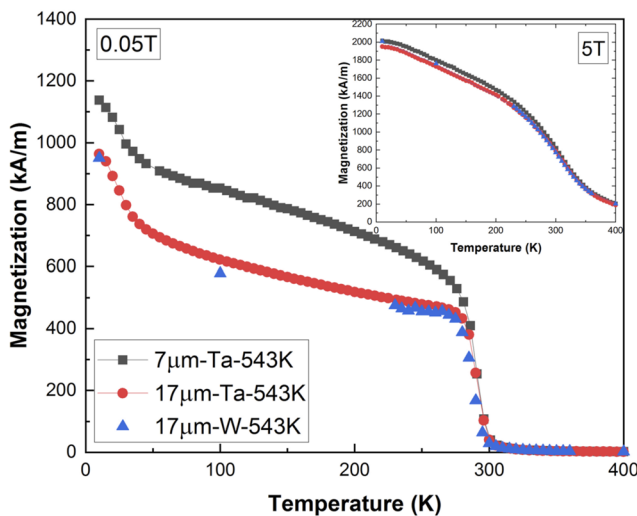


FIG. 5. Magnetization as a function of temperature under a 0.05 T (main frame) and a 5 T (inset) in-plane applied field.

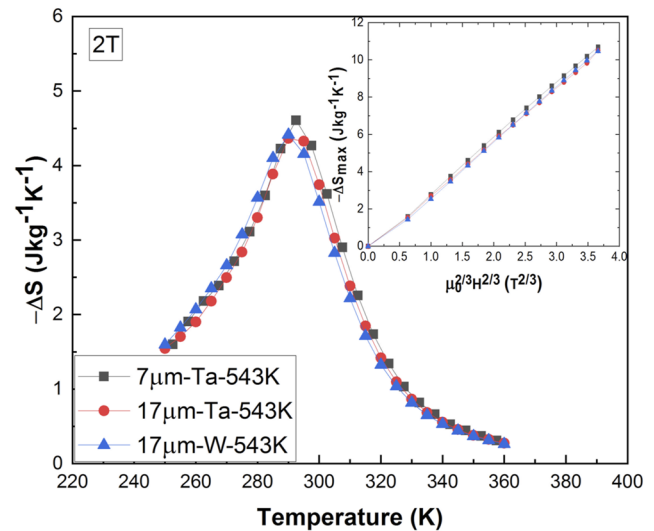


FIG. 6. Entropy change of freestanding films using Ta and W as buffer layers. The inset shows the plot of $(-\Delta S_{\text{max}})$ against $H^{2/3}$.

III. CONCLUSION

Fabrication of films for energy harvesting applications demands a full mastery of the magnetic properties, surface quality and flexibility. A full understanding of these key factors will pave the way to the use of thick magnetocaloric films in MEMS scale energy conversion devices, where magnetocaloric properties determine the conversion efficiency, and surface quality allows fast and reliable thermal transfer through solid-solid interfaces. Here, we show that freestanding films with good magnetic properties, notably showing an entropy change close to the one of bulk Gd, and high-quality surfaces can be obtained through a pretty simple mechanical substrate removal protocol. Surface morphology and magnetic properties are similar using Ta and W capping, however larger and thinner freestanding films are easier to obtain when using Ta as a buffer. We also point-out that while magnetic properties are improved by increasing growth temperature, above 550 K, high deposition temperature can negatively affect the film surfaces, a trade-off worth knowing to optimize the functional properties in view of specific applications.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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