Thin films of gadolinium investigated by photothermally modulated magnetic resonance

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Abstract. The photothermally modulated magnetic resonance (PM-MR) technique was used to study thin films of Gd grown on fused quartz substrates. With this technique it was possible to observe the magnetic phase transitions for samples with different thickness and thermal treatments. Results were correlated with both magnetization and ESR measurements. The effect of the stress induced by the substrate was clearly observed through peak of the PM-MR signal.

1. Introduction

Gadolinium has been considered of particular importance in potential applications of the magnetocaloric effect owing to its magnetic phase transition near to room temperature. The magnetocaloric effect is maximum around the phase transition, since the temperature rise produced by a given magnetic field variation is proportional to the temperature derivative of the magnetization. Thus, studies using different techniques can be useful. Unlike electron spin resonance (ESR) experiments, which yield a spatially averaged signal, the photothermally modulated magnetic resonance (PM-MR) technique can be used as a magnetic imaging tool for both laterally resolved and depth profile investigation of structured samples [1-3]. Furthermore, the PM-MR signal is dominated by the temperature derivative of the sample magnetization, $(\partial M/\partial T)$. Therefore, the technique can be useful for monitoring the local magnetocaloric behavior, regarding material heterogeneities produced by grain arrangement, compositional phases, stress induced by interface effects etc.

In this paper we use both the ESR and the PM-MR techniques to investigate gadolinium films deposited on fused quartz substrates with thicknesses varying from 1 µm to 3 µm. After deposition, samples were treated for 2.5 hours at 300 °C and 500 °C in vacuum. Resonance magnetic field, ESR linewidth and PM-MR peak were analyzed as a function of temperature around $T_C$ and compared with magnetization data.

2. Experimental aspects

The experimental PM-MR setup consists of a modified ESR spectrometer where the sample is exposed to a modulated focused laser beam, which produces temperature oscillations that modulate the
magnetic resonance through the temperature dependence of the magnetic parameters of the sample. In other words, the conventional field modulation is replaced by a temperature modulation which is used in the lock-in detection [1-3]. Both ESR and PM-MR measurements were performed with the external magnetic field oriented parallel to the surface of the samples, in the range from zero to 10 kOe. The front window of the microwave cavity was replaced by one with hole through which the laser beam passes. The temperature control was achieved with a Lakeshore system using nitrogen flow, and the measurements were done from 240 K to 320 K. An Ar+ laser beam operating at 514.5nm and modulated at 500 Hz was used for the temperature modulation, while a 100 kHz and 32 Oe ac magnetic field was employed in the ESR measurements.

The gadolinium films were deposited using sputtering technique at a 50nm/min rate. The thermal treatment at 300°C and 500°C was performed in vacuum for 2.5 hours. Magnetization measurements were carried out using a Quantum Design® Physical Properties Measurement System (PPMS).

3. Results and Discussion

Figure 1 shows the magnetization curves of the 3 µm samples under a constant magnetic field of 500 Oe. From these measurements one can find the transition temperatures as ~277 °C for the non-treated sample, and ~289 °C and ~295 °C for those treated at 300 °C and 500 °C, respectively. The influence of the substrate on the film characteristics includes the decreasing of the transition temperature with respect to the bulk material. Thermal treatment partially restores the bulk characteristics, through stress suppression, thus shifting up the transition temperature. The same trend was observed in the case of the 1 µm Gd film. In that case the corresponding transition temperatures were ~272 °C, ~287 °C and ~295 °C, revealing an enhanced effect of the substrate, as expected.

The behavior of the ESR and PM-MR signals for the 3 µm thickness non-treated sample can be seen in Fig. 2. In both techniques it is possible to observe the region where the phase transition occurs. However, it is easier to see the phase transition in the PM-MR curves, since the signal has a maximum around Tc, clearly related to the (∂χ/∂T)H behavior. This main behavior is observed in all the six studied samples.

Figure 1. Normalized magnetization for the 3 µm thickness Gd films.

The general form for the microwave absorption curves for these materials is the dysonian, function of both the real and the imaginary parts of the susceptibility, χ. In the ESR case, since a small modulated magnetic field is superimposed on a dc one, the measured spectrum is proportional to (∂χ/∂H)T. On the other hand, the PM-MR signal is due to the difference between two absorption curves related to two temperatures, i. e., it is proportional to (∂χ/∂T)H.

From the data fitting of the ESR spectra, both the resonance magnetic field (H0) and the linewidth (ΔH0) were obtained as a function of the temperature. Figure 3 shows the H0 and ΔH0 parameters for the 3 µm samples. From this figure, one can see that the resonance magnetic field shifts up in the phase transition, increasing from hundreds of Oe in the ferromagnetic phase to 3.0 kOe in the paramagnetic one. At the same time the linewidth decreases from about 1 kOe to 0.5 kOe. In addition, the thermal treatment shifts the curves H0 vs. T and ΔH0 vs. T towards higher temperatures. Similar behavior is found in the 1 µm thickness samples. The peak in the ΔH0 curve for the 3 µm sample treated to 500°C is possibly associated with fluctuations in the phase transition.
Using the values of $H_0$ and $\Delta H_0$, as well as their dependences with temperature, it was possible to simulate the PM-MR signal, resulting in curves in very good agreement with the experimental spectra. Figure 4 presents an example such simulated curves.

In order to clearly display the correlation between the PM-MR signal and the magnetization and ESR data, the maximum value of the PM-MR spectrum for each temperature is plotted against temperature for the six investigated sample in Fig. 5 (top part). For the sake of comparison, the temperature derivatives of the magnetization are also plotted in the same figure, showing the $T_C$ values at their minima (bottom part). As one can see, the PM-MR normalized peaks present a maximum value around $T_C$, shifting to higher
temperatures as samples are thermally treated. Besides, the linewidth of these normalized peak curves decreases as thickness and thermal treatment temperature increases.

This is probably caused by heterogeneity along the film thickness induced by the substrate interface. As the thickness increases, and the sample is thermally treated, the film becomes homogeneous, localizing the phase transition temperature, and therefore narrowing the normalized peak curves.

![Normalized peak curves for different thicknesses and temperatures](image)

**Figure 5.** Comparison between the normalized peak of the PM-MR signal amplitude and the temperature derivative of the magnetization for the set of six investigated samples.

4. Conclusions

In this paper we show that the PM-MR is a powerful technique for the study of magnetic phase transition, owing to its direct dependence on $\frac{\partial M}{\partial T}$. Furthermore, its spatial resolution ability may be used to discriminate among contributions coming from different parts of the sample. Particularly, a depth profile can be obtained through a frequency scan, which would evidence the interface influence on the Gd film structure.

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