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Growth and characterization of Pt-protected Gd_5Si_4 thin films

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Successful growth and characterization of thin films of giant magnetocaloric $Gd_5(Si_xGe_{1-x})_4$ were reported in the literature with limited success. The inherent difficulty in producing this complex material makes it difficult to characterize all the phases present in the thin films of this material. Therefore, thin film of binary compound of Gd_5Si_4 was deposited by pulsed laser deposition. It was then covered with platinum on the top of the film to protect against any oxidation when the film was exposed to ambient conditions. The average film thickness was measured to be approximately 350 nm using a scanning electron microscopy, and the composition of the film was analyzed using energy dispersive spectroscopy. X-ray diffraction analysis indicates the presence of Gd_5Si_4 orthorhombic structure along with Gd_5Si_3 secondary phase. The transition temperature of the film was determined from magnetic moment vs. temperature measurement. The transition temperature was between 320 and 345 K which is close to the transition temperature of the bulk material. Magnetic moment vs. magnetic field measurement confirmed that the film was ferromagnetic below 342 K. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4865322]

I. INTRODUCTION

$Gd_5(Si_xGe_{1-x})_4$ compound has been broadly studied,[1–4] yet all of the past research has been concerned with *bulk* materials. *Thin films* of these strain sensitive materials, if they can be reproducibly prepared and protected from oxidation under ambient conditions, will open up new science ranging from strain controlled magnetism to functionally graded materials. Previous attempts to prepare thin films of this alloy system have all resulted in failure[5] because of high melting points of the compounds, incongruent melting, and extreme difficulties in controlling oxygen content during and after deposition. Our initial work[6] showed high probability of success, even though the prepared films contained multiple phases. Importantly, the monoclinic $Gd_5Si_2Ge_2$ phase has been identified. In the present work, we have deposited a thin film of Gd_5Si_4 and protected it from oxidation by pulsed laser deposition (PLD) of 10–20 nm platinum using a femtosecond laser.

High purity bulk Gd_5Si_4 sample was used as the target material. The laser was repositioned on platinum without breaking the vacuum and a 10–20 nm layer of platinum was deposited on top of the Gd_5Si_4 thin film. Microstructure analysis using scanning electron microscopy (SEM), Energy Dispersion X-ray Spectroscopy (EDS) was carried out to determine the film thickness, morphology, and composition. Magnetic moment vs. temperature measurements were carried out at an applied field of 500 Oe. The sample showed a major transition below 150 K and a minor transition around 335 K similar to the bulk sample. Magnetization measurements at 5 K and 300 K showed similar magnetic field needed to saturate M as in the bulk material.

II. SAMPLE PREPARATION AND EXPERIMENTAL DETAILS

A polycrystalline Gd_5Si_4 sample prepared by arc melting using ultrapure grade gadolinium was used as a target in the pulsed laser deposition. Spectra Physics' Solstice femtosecond laser with a repetition rate of 1000 Hz, pulse energy of up to 3.5 mJ, and a nominal beam diameter of 7 mm before focussing was used for the deposition. The film was deposited on a (001) SiO_2 substrate at 300 °C at a pressure of 1.2×10^{-6} Torr. Secondary Electron (SE) detector and Back Scattered Electron (BSE) detectors were used during SEM imaging. X-ray diffraction (XRD) was carried out in a PANanalytical equipment with a Co X-ray tube. The XRD data were analyzed in FullProf software. Magnetization measurements were carried out on a SQUID magnetometer.

III. RESULTS AND DISCUSSIONS

Pulsed laser deposition using a femto-second laser has been widely used for Coulomb ablation where the high pulse rate of the laser's photon repeatedly excites an electron before it falls back to the ground state thus eliminating the phonon generation from the process. Since Coulomb ablation is a cold process, the resultant deposited films are smoother and have smaller particle sizes. Figs. 1(a) and 1(b) show secondary electron images of the film at magnifications at 15 000x and 100 000x, respectively. The deposition shows a continuous film with varying sizes of spherical particles

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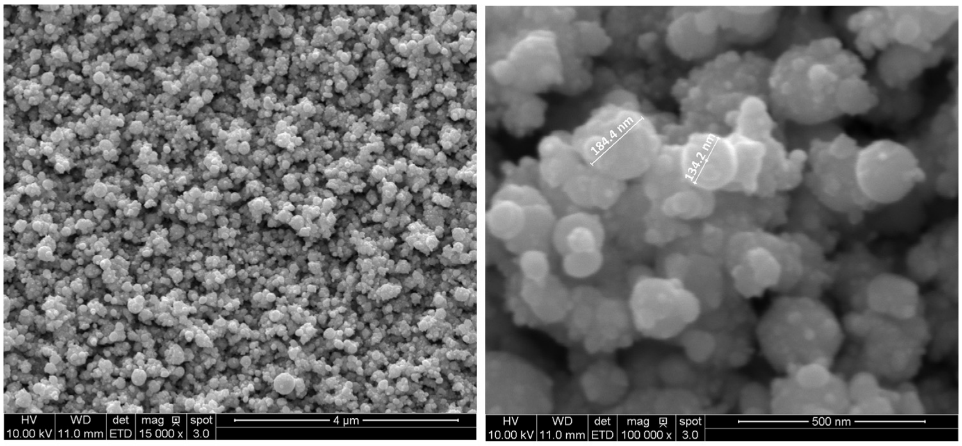
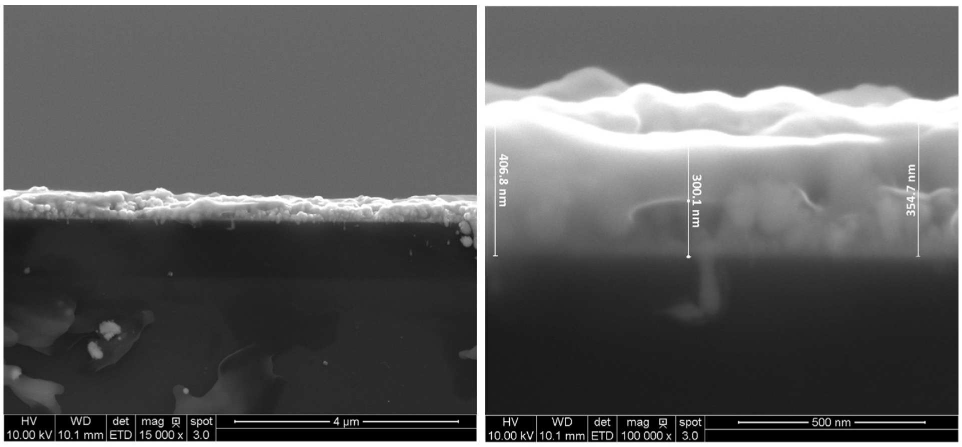


(a) (b)

FIG. 1. Microstructures of thin film: (a) secondary electron image at 15 000x and (b) secondary electron image at 100 000x showing spheres of average size of about 150 nm.



(a) (b)

FIG. 2. Cross section microstructures of thin film: (a) secondary electron image at 15 000x and (b) secondary electron image at 100 000x showing the average thickness of the film of 350 nm.

which is typical of any pulsed laser deposition.[7] The average particle size of the film was about 150 nm. The film also showed an Root Mean Square (RMS) roughness value of about 75 nm as shown in the supplementary Fig. 7.[8]

Fig. 2(a) shows the cross-section of the film that is continuous at 15 000x magnification. The thickness of the film was measured at 100 000x magnification as shown in Fig. 2(b). Average thickness of the film was approximately 350 nm. Fig. 3 shows the EDS taken at the three different locations on the film. Peaks of Gd and Si from all the three regions match closely with respect to the intensity suggesting similar composition. Quantitative analysis of the composition was carried out, where the K (1.74 keV) and M (1.2 keV) lines of silicon and gadolinium were used for quantification. In order to eliminate electrons from the electron gun penetrating into the substrate, we have used a 10 keV accelerating voltage which was determined by Monte Carlo simulation of electron penetration depth. It was observed that regions that have low platinum content on the film showed high oxygen indicating that platinum is protecting the underlying film.

XRD measurement of Pt-protected Gd_5Si_4 thin films was also carried out. Peaks of Gd_5Si_4 type orthorhombic structure and peaks of Gd_5Si_3 type hexagonal structure were first generated using PowderCell software and compared with the experimental data. Peaks are then identified in the spectra as shown in Fig. 4. However, peaks of platinum were not present due to the low concentration of Pt.

Magnetic moment as a function of temperature was measured at an applied field of 1000 Oe (79.58 kA/m) as shown in Fig. 5. The film shows 2 magnetic transitions in the measurement; a major transition between 10 K and 150 K and a minor transition between 320 K and 345 K. The minor transition corresponds to a second order phase transition of the Gd_5Si_4 phase,[1] and the major transition between 10 K and 150 K may be the transition temperature of two or more phases including Gd_5Si_3 phase that has a transition temperature of 78 K.[9]

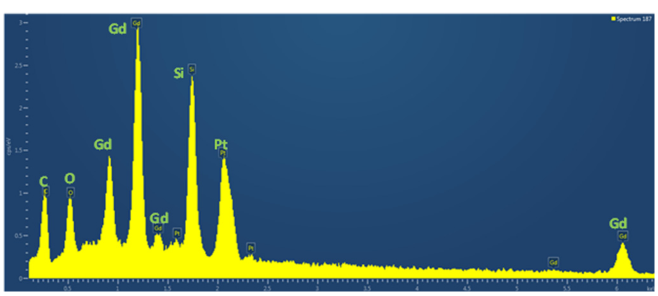


FIG. 3. EDS peaks on different locations of the thin film indicating same peaks with similar intensities of thin film of Gd_5Si_4 with platinum protection on top.

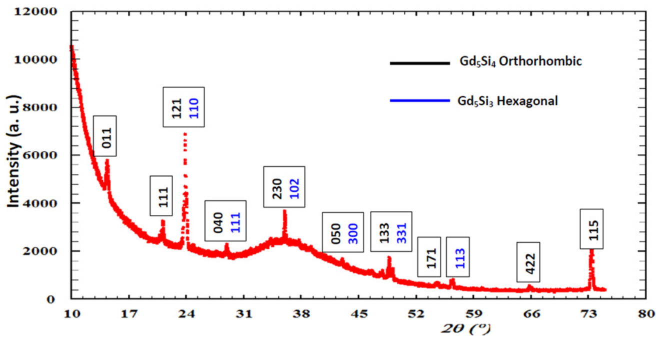


FIG. 4. XRD of think film of Gd_5Si_4 compared with peaks of Gd_5Si_4 orthorhombic structure and Gd_5Si_3 hexagonal structure and identified in the spectra.

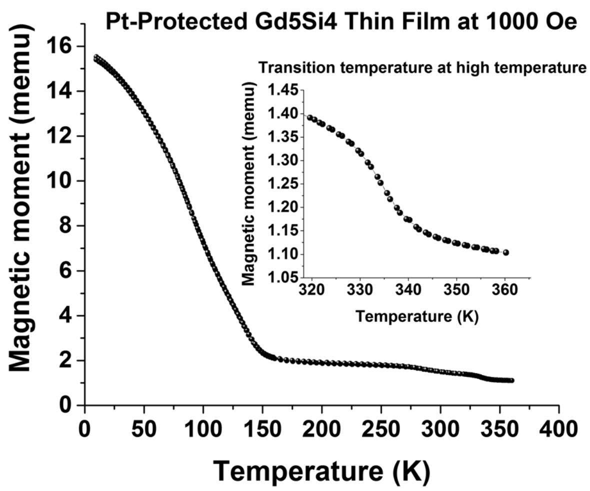


FIG. 5. m vs. T at an applied field of at 1000 Oe (79.58 kA/m) showing presence of two transitions; a minor transition of Gd_5Si_4 phase between 320 K and 345 K (inset) and a major broad transition between 10 and 150 K from two or more phases in the film.

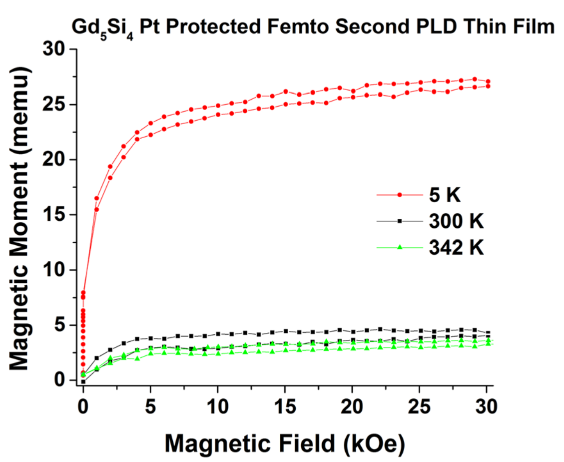


FIG. 6. m vs. H at 5 K, 300 K, and 342 K showing the ferromagnetic nature of the film with a saturation magnetic field of 5 kOe (0.397 MA/m).

Fig. 6 shows magnetic moment vs. magnetic field at 5 K, 300 K, and 342 K. It can be seen that the sample is ferromagnetic at 5 K and 300 K and saturates below 5 kOe (0.397 MA/m). The isotherm 342 K also shows ferromagnetic behavior as the sample is not completely paramagnetic. Our previous work[6] on deposition of $Gd_5Si_{2.09}Ge_{1.91}$ without a protective layer of pt was difficult to characterize as the sample would have had gadolinium silicide, galolinium germanide, gadolinium oxide, and pure gadolinium phases. It was also difficult to confirm the transition temperature close to 290 K was the transition of $Gd_5Si_{2.09}Ge_{1.91}$ or of pure gadolinium. With the current work, it is now confirmed that the transition occurring at high temperature is the transition temperature of the target material.

IV. CONCLUSION

A magnetic thin film of Gd_5Si_4 was successfully grown with a platinum protective layer. Its microstructure was analyzed using SEM and the composition of the film was determined by EDS. It showed higher oxygen content in the regions with lower platinum. XRD analysis showed the presence of orthorhombic Gd_5Si_4 and hexagonal Gd_5Si_3. Magnetic moment vs. temperature measurements on a thin film showed a minor phase transition at temperature similar to the phase transition temperature of the bulk material and a major transition occurring over a broad temperature range between 10 K and 75 K indicating two or more phases were present in the film. Magnetic moment vs. magnetic field measurements on the thin film at different temperatures showed that the magnetization in the film saturated close to a field of 5 kOe (0.397 MA/m).

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