2013

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Abstract

We report for the first time successful growth of magnetic thin films containing the Gd5(Six Ge1−x)4 phase, which is expected to show giant magnetocaloric properties. The film wasdeposited by Pulsed Laser Deposition (PLD) on a (001) silicon wafer at 200 °C from a polycrystalline Gd5Si2.09 Ge 1.91 target prepared by arc melting. PLD was achieved using a femto second laser with a repetition rate of 1 kHz, and a pulse energy of up to 3.5 mJ. The average film thickness was measured to be 400 nm using a Scanning Electron Microscopy and the composition of the film was analyzed using Energy Dispersive Spectroscopy and found to be close to the target composition. X-Ray Diffraction analysis confirmed the presence of Gd5Si2Ge 2 monoclinic structure. Magnetic moment vs. magnetic field measurement confirmed that the film was ferromagnetic at a temperature of 200 K. The transition temperature of the film was determined from a plot of magnetic moment vs. temperature. The transition temperature was between 280 and 300 K which is close to the transition temperature of the bulk material.

Keywords

Ames Laboratory, Germanium, Pulsed laser deposition, Thin films, Magnetic films, Magnetic moments

Disciplines

Electromagnetics and Photonics

Comments

The following article appeared in *Journal of Applied Physics* 113 (2013): 17A935 and may be found at http://dx.doi.org/10.1063/1.4799975.

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Citation: Journal of Applied Physics **113**, 17A935 (2013); doi: 10.1063/1.4799975
View online: http://dx.doi.org/10.1063/1.4799975
View Table of Contents: http://scitation.aip.org/content/aip/journal/jap/113/17?ver=pdfcov
Published by the AIP Publishing

JOURNAL OF APPLIED PHYSICS **113**, 17A935 (2013)

Growth and characterisation of $Gd_5(Si_xGe_{1-x})_4$ thin film

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(Presented 16 January 2013; received 1 November 2012; accepted 24 January 2013; published online 9 April 2013)

We report for the first time successful growth of magnetic thin films containing the $Gd_5(Si_xGe_{1-x})_4$ phase, which is expected to show giant magnetocaloric properties. The film was deposited by Pulsed Laser Deposition (PLD) on a (001) silicon wafer at 200 °C from a polycrystalline $Gd_5Si_{2.09}Ge_{1.91}$ target prepared by arc melting. PLD was achieved using a femto second laser with a repetition rate of 1 kHz, and a pulse energy of up to 3.5 mJ. The average film thickness was measured to be 400 nm using a Scanning Electron Microscopy and the composition of the film was analyzed using Energy Dispersive Spectroscopy and found to be close to the target composition. X-Ray Diffraction analysis confirmed the presence of $Gd_5Si_2Ge_2$ monoclinic structure. Magnetic moment vs. magnetic field measurement confirmed that the film was ferromagnetic at a temperature of 200 K. The transition temperature of the film was determined from a plot of magnetic moment vs. temperature. The transition temperature was between 280 and 300 K which is close to the transition temperature of the bulk material. © *2013 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4799975]

I. INTRODUCTION

Magnetocaloric $Gd_5(Si_xGe_{1-x})_4$ has been studied extensively, since the giant magnetocaloric effect was discovered by Pecharsky *et al*.[1] Various other rare earth materials were also studied by the same group in search of even higher giant magnetocaloric effect.[2] Bruck *et al*. reported giant magnetocaloric effect in non-rare earth materials ($MnFeP_{0.45}As_{0.55}$) at room temperature.[3] There has been extensive work on bulk magnetocaloric materials[1–7] but there are fewer reports on thin films or other nanostructured magnetocaloric materials, although thin films of magnetocaloric materials have potential applications in micro-cooling in ICs and MEMS. Sambandam *et al*.[8] reported unsuccessful growth of $Gd_5Si_2Ge_2$ thin film at a higher temperature of 750–1150 °C using sputtering technique on a silicon nitride wafer.

In this paper we report successful growth of magnetic thin film of $Gd_5Si_{2.09}Ge_{1.91}$ using Pulsed Laser Deposition (PLD) technique and its structural and magnetic characterization. The film's microstructure including the thickness was analyzed using Scanning Electron Microscopy (SEM) and the composition was determined by Energy Dispersive Spectroscopy (EDS). Magnetic measurements and X-ray diffraction (XRD) of the film were also analyzed.

II. SAMPLE PREPARATION AND EXPERIMENTAL DETAILS

A polycrystalline $Gd_5Si_{2.09}Ge_{1.91}$ sample prepared by arc melting using commercial 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 being focused was used for the deposition. The film was deposited on a (001) silicon wafer at 200 °C at a pressure of 1.2×10^{-6} Torr. The deposition was carried out for 20 min. The rate of deposition was estimated from the thickness measurement and found to be 20 nm/s. Microstructure and composition analyses were carried out using SEM and EDS, respectively. Secondary Electron (SE) detector and Back Scattered Electron (BSE) detectors were used during SEM imaging. XRD was carried out in the PANanalytical equipment with a Cu X-ray tube. The XRD data were analyzed in X'PERT HIGHSCORE software. Magnetization measurements were carried out on a SQUID magnetometer.

III. RESULTS AND DISCUSSIONS

Figs. 1(a) and 1(b) show SE and BSE images of the film at magnifications at 1500 × and 15000 ×, respectively. The deposition shows a continuous film with varying sizes of spherical droplets which is the characteristic of PLD deposition of metallic thin films. Femtosecond laser was chosen for this deposition as the shorter pulse width produce smaller droplets and smoother films.[9] With a repetition rate of 1000, higher deposition rate is achieved at lesser time which helps to obtain similar phase material to the target material. BSE image shows most of the top grains in one gray level and the grains in the bottom layer with a different grey level. This variation in the contrast between the grains at different thickness of the film may be due to different phases of the material. However, another reason could be that variation in the distance between grains and the detector also results in different contrast in the BSE image. Fig. 1(c) shows the cross-section of the film that is continuous at 15000 × magnification. Thickness of the film was measured at 30000 × magnification as shown in Fig. 1(d). Minimum thickness was measured to be 232 nm and maximum was 616 nm. Using the

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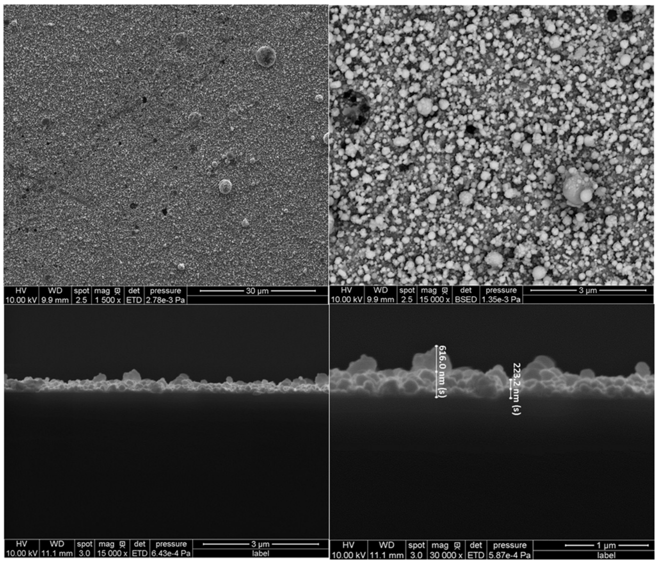

FIG. 1. (a) Secondary electron image at 1500 ×, (b) BSE image at 15000 ×, (c) cross section of thin film at 15000 ×, and (d) thickness measurement on cross section at 30000 ×.

thickness measured from Fig. 1(d) the deposition rate was estimated to be 20 nm/s. EDS was carried out at three different locations on the film. The locations were chosen on three spherical particles of different sizes. Peaks of Gd, Si, and Ge from all the three spherical particles match closely with respect to the intensity suggesting similar composition. Table I shows quantitative analysis of composition, where the K(1.74 keV), K(9.8 keV), and L(6.05 keV) lines of silicon, germanium, and gadolinium were used for quantification. The composition of the film was similar to the composition of the target. The L line of germanium and the M line of gadolinium overlap at 1.2 keV, which cannot be used for quantification of composition, hence the K line of germanium and the L line of gadolinium were used. In order to get the K line (9.8 keV) of germanium the accelerating voltage of the electron should be about 15 kV. Electrons penetrate into the wafer when the accelerating voltage of the electron is high and EDS detector detects x-rays that are emitted by the wafer. CASINO simulation software was used to determine the thickness of the film such that minimum number of electrons penetrates into the substrate which was determined to be about 150 nm for our parameters.

XRD analysis of thin film of $Gd_5Si_{2.09}Ge_{1.91}$ was carried out at room temperature. X'PERT HIGHSCORE PLUS software was used to identify and match the peaks. This search and match function indicated the presence of other phases such as Gd_5Si_4 and Gd_5Ge_3 as shown in Table II.

Magnetic moment vs. temperature was measured at an applied field of 100 Oe (7.9 kA/m) as shown in Fig. 2(a),

TABLE I. Composition of the film averaged from 3 locations.

Element	Line type	Wt. %	Wt. % sigma	At. %
Si	K	6	0.12	23
Ge	K	14	0.75	22
Gd	L	80	0.71	55
Total:		100.0		100.0

TABLE II. X'PERT HIGHSCORE PLUS matched structures of $Gd_5Si_2Ge_2$ Gd_5Ge_3 and Gd_5Si_4.

Ref. code	Score	Compound name	Scale factor	Chem formula
01-087-2320	24	Gadolinium silicide germanide	0.317	$Gd_5(Si_2Ge_2)$
00-026-1421	14	Gadolinium germanium	0.283	Gd_5Ge_3
01-087-2319	21	Gadolinium silicide	0.512	Gd_5Ge_4

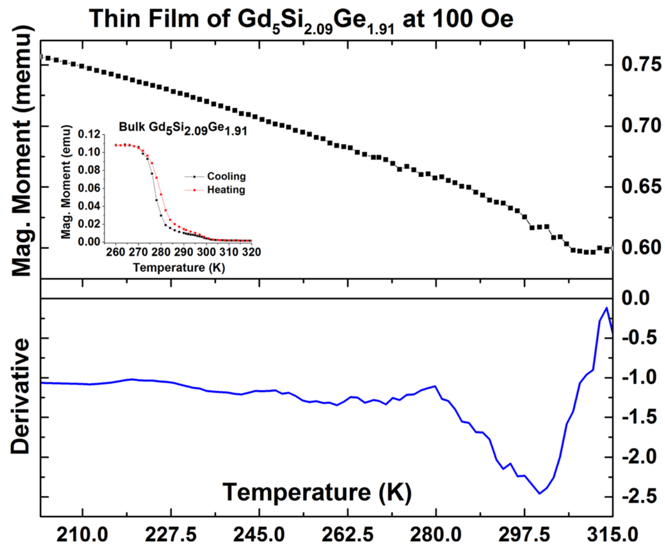

FIG. 2. (a) m vs. T at an applied field of at 100 Oe (7.9 kA/m). (b) Derivative of Fig. 2(a) showing the start and end of the phase transition. Inset figure shows the transition temperature of bulk sample of $Gd_5Si_{2.09}Ge_{1.91}$.

with its derivative shown in Fig. 2(b). It can be seen that there is a constant slope below 280 K and then its value increases from 280 K to 300 K indicating that there is a phase transition occurring between these temperatures.[10,11] The volume fraction of the monoclinic phase was estimated from the magnetic moment variation at the transition temperature and found to be 11% of the original material considering that other phases do not have a transition temperature below 200 K.

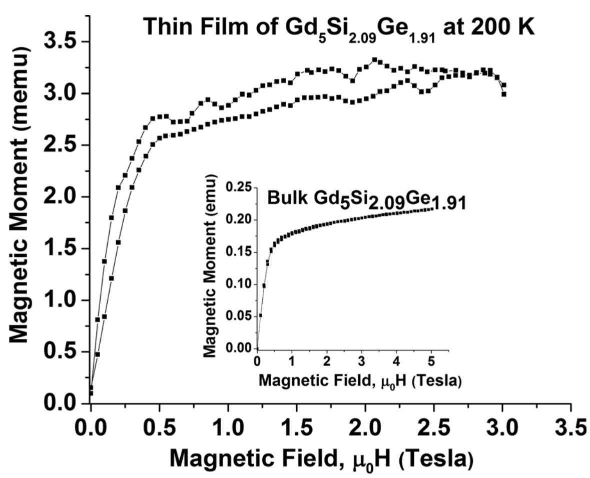

FIG. 3. m vs. μ_0 H at 200 K showing the ferromagnetic nature of the material inset figure shows m vs. H measurement at 270 K on bulk sample of $Gd_5Si_{2.09}Ge_{1.91}$.

The transition temperature of the same composition measured on the bulk material at the same 100 Oe (7.9 kA/m) is between 270 K and 300 K as shown in the inset. Fig. 3 shows magnetic moment vs. magnetic field at 200 K. It can be seen that the sample is ferromagnetic and saturates below 0.5 T (0.39 MA/m). The inset shows the magnetization of the bulk sample with composition $Gd_5Si_{2.09}Ge_{1.91}$ at 270 K which also saturates at a similar magnetic field.

IV. CONCLUSION

A magnetic thin film of $Gd_5(Si_xGe_{1-x})_4$ phase was successfully grown for the first time that is expected to show giant magnetocaloric properties. Its microstructure was analyzed using SEM. The composition of the film was determined by EDS using non-overlapping principal lines. XRD analysis confirmed the presence of monoclinic $Gd_5Si_2Ge_2$ structure. The magnetic moment vs. temperature measurements on a thin film and a bulk sample showed similar phase transition temperatures. Magnetic moment vs. magnetic field measurements on thin film and bulk samples also showed that saturation is reached at similar values of magnetic field.

ACKNOWLEDGMENTS

This work at the Ames Laboratory was supported by the DOE-Basic Energy Sciences under Contract No. DE-AC02-07CH11358 and Barbara and James Palmer Endowment at the Department of Electrical and Computer Engineering of Iowa State University. The authors acknowledge the contributions of A. H. Shaw and K. W. Dennis Ames Laboratory, US DOE for helping with the PLD and SQUID measurements, respectively.

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