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Effects of preparation conditions on the magnetocaloric properties of Gd thin films

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The impact of the deposition temperature and chamber gettering on Ta(5 nm)/Gd(30 nm)/Ta(5 nm) thin films magnetocaloric effect properties was investigated. Increasing the deposition temperature generally improves the entropy peak (magnitude, full width at half max, and temperature of the peak) but also leads to significant oxidation. Gettering the chamber prior to deposition not only reduced this oxidation issue but also increased the relative cooling power of films grown at elevated temperatures by as much as 33% over ungettered samples. © *2013 American Vacuum Society*. [http://dx.doi.org/10.1116/1.4795817]

I. INTRODUCTION

The magnetocaloric effect (MCE) is a phenomenon where a magnetic material exhibits a temperature or entropy change when subjected to a magnetic field variation[1] and was discovered over 100 years ago by German physicist Emil Warburg.[2] The effect is often used in refrigeration cycles where temperatures as low as 0.25 K are achieved in a process of adiabatic demagnetization.[3,4] As the material undergoes adiabatic demagnetization, the total entropy of the system will be conserved. The total entropy includes the entropy of the lattice and the entropy related to the magnetic moment of the magnetic material. As the material is magnetized, the magnetic moments of the ferromagnetic material orient themselves in the direction of the applied field. The alignment of the moments causes a decrease in the spin entropy and as a consequence the lattice entropy is increased. This increase in lattice entropy heats the material. This excess heat is then removed by heat exchange with a cooler body, and the applied field is removed. The removal of the applied field causes the magnetic moment entropy to increase and the lattice entropy to decrease.[5] The decrease in lattice entropy cools the material and can be used to refrigerate.[6]

Compared to conventional gas compression technology,[7] magnetic refrigeration technologies have advantages such as eliminating the need for energetically inefficient compressors, lack of moving parts, and lack of volatile liquid refrigerants.[1] Magnetic refrigerators can be more compactly built when using solid substances as working materials.[8] Since the heat transfer during the refrigeration process is dependent upon the entropy change in the magnetic refrigerant element,[6] a material system exhibiting a large entropy change is highly advantageous to magnetic refrigeration technologies. An entropy change can be induced in magnetic refrigerant materials by either magnetic or structural phase transition, provided that a difference in the magnetization exists between the initial and final phases. Current research is focused on materials (bulk alloys,[9–12] Gd alloys,[13,14] thin film superlattices,[15] or nanocomposites[16,17]) that are cost effective and exhibit large relative cooling power (RCP), which is a measure of the amount of heat transfer between the cold and hot sinks in an ideal refrigeration cycle.[6] Gadolinium has been the standard for magnocaloric materials[18] and has been used in a proof-of-principle magnetic refrigerator demonstrating that magnetic refrigeration is a viable and competitive cooling technology in the near room temperature region with potential energy savings of up to 30%.[19,20]

II. EXPERIMENT PROCEDURE

Samples with the nominal structure Ta(5 nm)/Gd(30 nm)/Ta(5 nm) were grown on oxidized silicon (100) wafers by magnetron sputtering in a system whose base pressure was approximately 30 nTorr. Thin Ta (5 nm) is a very common seed layer thickness for thin film growth because the Ta is amorphous at this thickness, allowing for smooth substrate for subsequent layers. In this particular case, Ta and Gd are immiscible, which makes a sharp interface between the materials. Also, the buffer layer acts as a barrier to oxidation of the Gd film from the SiOx layer. The capping layer of 5 nm of Ta was used to prevent oxidation of the Gd films once they were exposed to atmosphere for structural and magnetic measurements.[21] The samples were deposited in 3 mTorr of ultra high purity Ar gas, using 99.99% purity Ta and 99.95% rare earth equivalent Gd targets at 100 W DC and RF, respectively. A liquid Nitrogen cold trap was used to reduce the amount of water vapor in the sputtering chamber.

Two sample sets were grown, each containing samples deposited at temperatures from room temperature up to 600 °C in 150 °C increments. The films were grown in a random order (rather than ascending or descending temperatures) in order to separate any temporal effects (i.e., chamber variations) from actual effects of growth temperature. The difference between the two sample sets was whether or not the films were grown after gettering the chamber. The gettering process consisted of bringing a blank sample holder up to 600 °C for 30 min and then sputtering Gd for 30 min at 3 mTorr prior to the deposition of the gettered films in order to react with any residual oxygen left in the chamber. Subsequent to the gettering procedure, the temperature was

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allowed to cool down to below 150 °C after which the deposition of each sample commenced at the desired temperature.

III. RESULTS AND DISCUSSION

Structural analysis of these samples was done using wide angle x-ray diffractometry (XRD) and x-ray reflectivity (XRR) measurements using a Bruker D8 Focus diffractometer with Cu k-α radiation. The XRD patterns of the ungettered and gettered films are shown in Fig. 1. We have found that the bcc β-phase grows preferentially over the bulk hcp α-phase in thin film Gd. The ungettered XRD data showed that generally the Gd oxide phases seem to increase as the deposition temperature was increased. The fcc Gd_2O_3 (111) and bcc Gd (110) were the dominant phases in most of the samples with fcc GdO (111) being the dominant phase in the 600 °C sample. The d spacing of the bcc Gd (110) and fcc Gd_2O_3 (111) were 0.29 and 0.31 nm, respectively. There appeared to be no elemental Gd in the 600 °C ungettered film.

The gettered XRD data showed that the dominant phases of most these films were also bcc Gd (110) and fcc Gd_2O_3 (111) with similar d spacings as the ungettered films. However, unlike the ungettered film grown at 600 °C, the bcc Gd (110) phase was present as were fcc GdO (111) and fcc Gd_2O_3 (111). The fcc phase of Gd (200) appeared in relatively small quantities at deposition temperatures above 300 °C and had a d spacing of 0.55 nm for the gettered films grown at 450 and 600 °C. This fcc phase of Gd was not observed in any of the ungettered films. It appears that gettering improves the structural formation of the Gd cubic phases, while increasing the substrate temperature favors oxide formation. The Gd oxide present in the samples increased with increasing deposition temperature. This is illustrated by Fig. 2, in which the ratio of the integrated areas of the Gd (110) peak to the Gd_2O_3 (111) peak is plotted versus deposition temperature.

The XRR data are shown in Fig. 3. The higher frequency oscillations are due to the Gd, and the low frequency oscillations are due to the thinner Ta. The average thicknesses inferred from the reflectivity data for the ungettered and gettered sets were 33.2 and 31.1 nm, respectively. The ungettered

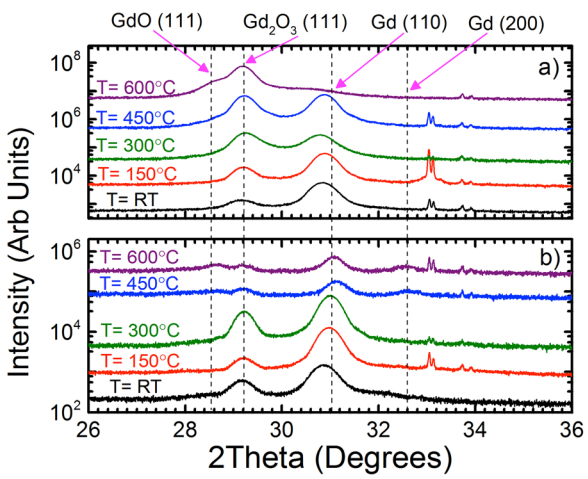

FIG. 1. (Color online) Wide angle diffraction data for (a) the ungettered set and (b) the gettered set. The peaks at 33° are due to the substrate.

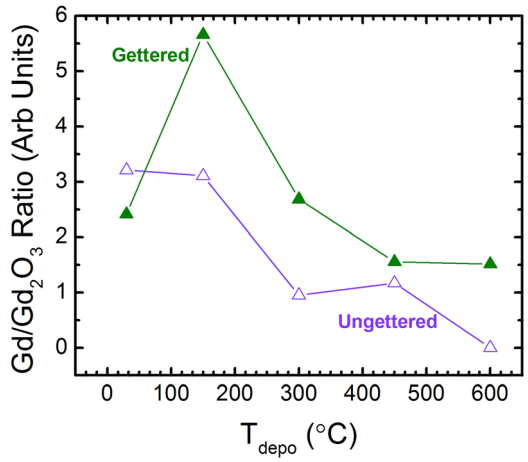

FIG. 2. (Color online) Ratio of the Gd (110) peak to the Gd_2O_3 (111) peak for the ungettered (purple, open symbols) and the gettered (green, closed symbols) films. With the exception of the films grown at room temperature, the gettered films had a larger amount of Gd present.

samples have the high frequency oscillations preserved to 450 °C. The 600 °C sample was purely oxide and had a rougher sample surface. The gettered samples, however, have the high frequency oscillations preserved to only 300 °C. The gettered film grown at 450 °C had larger interface roughnesses than the ungettered film grown at the same temperature as indicated by the absence of the high frequency oscillations. This is also the temperature at which the fcc phase appears in the wide angle XRD. The coexistence of the two phases seems to increase the surface roughness.

Magnetic properties were carried out using a Quantum Design Physical Property Measurement System with a vibrating sample magnetometer attachment. Isothermal magnetization (M–H) curves were measured in persistent mode using a 20 Oe/s sweep rate and a 5 s averaging time using a vibrating sample magnetometer. The temperatures used ranged from 180 to 330 K, in 10 K increments. The magnetization data were normalized to the nominal Gd mass of each sample, which was calculated by the product of the sample area, Gd thickness measured via XRR, and the bulk density of Gd.

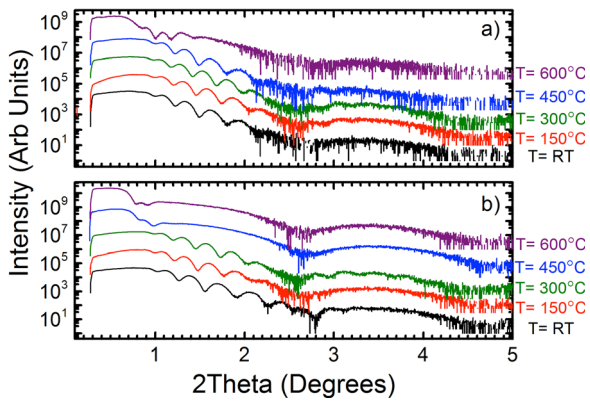

FIG. 3. (Color online) Low angle diffraction data for (a) the ungettered set and (b) the gettered set. Within each set, the intensity of the high frequency oscillations which are due to the Gd layer fade as T_{depo} was increased. In the gettered set, the structural formation of the bcc Gd(110) phase as well as the fcc Gd(200) phase seems to cause a rougher film surface for the films deposited at 450 and 600 °C as indicated by the loss of high frequency oscillations.

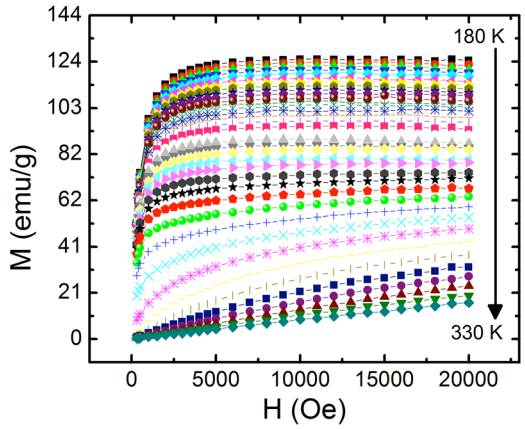

FIG. 4. (Color online) Isothermal magnetization as a function of field for the gettered film deposited at 450 °C. The temperature ranged from 180 to 330 K in 10 K steps.

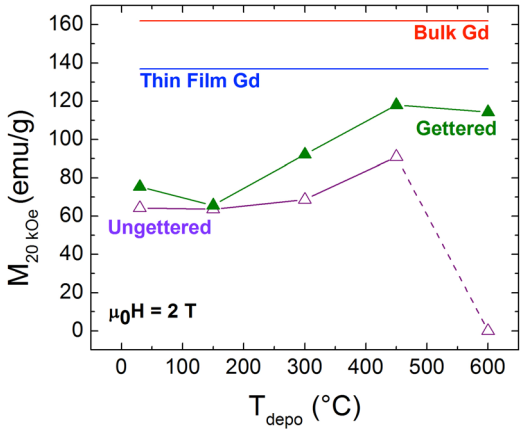

FIG. 5. (Color online) Magnetization at 20 kOe ($M_{20\ kOe}$) as a function of deposition temperature for both ungettered and gettered films at $\mu 0\,H = 2\,T$ at 220 K. Generally, $M_{20\ kOe}$ increased as a function of deposition temperature and was larger in the gettered set. The (top, red) horizontal line is the $M_{20\ kOe}$ of a bulk piece of Gd and the (bottom, blue) horizontal line is the $M_{20\ kOe}$ of thin film Gd from Ref. 23.

The $-\Delta S$ versus temperature curves were measured by using isothermal M–H curves and the second order Maxwell relation, $-\Delta S_m(T) = \int [(\partial M(T,H)/\partial T)]_H\, dH$. The RCP is the product of the full width at half max (FWHM) and the peak value of the resulting $-\Delta S$ curves. The magnetometry data are summed up in Figs. 4–7.

The M–H curves for the gettered film deposited at 450 °C are shown in Fig. 4. The paramagnetic background (from the Ta layers) and the diamagnetic background (dominated by the substrate) from the sample measured at 180 K were subtracted from each isotherm shown. This is a valid approximation under the assumption that these contributions are temperature independent in the range of temperatures of interest. However, since the Gd is still relatively close to its phase transition, even bulk Gd does not become field independent at these temperatures at tesla-levels of magnetic field. Thus, while we present the data in Fig. 4 as saturated, the reader should be cognizant of this caveat. Fortunately, the derivative with respect to temperature in the entropy calculation intrinsically removes the impact of these temperature-independent background signals, and we are not required to do any subtraction for analyzing the magnetocaloric properties. These data werea general representation of the samples in each respective set with the exception of the ungettered sample deposited at 600 °C. This ungettered film was determined to be diamagnetic, which makes sense since the XRD data showed only GdO (111) (Fig. 1).

Figure 5 shows that the magnetization at 20 kOe ($M_{20\ kOe}$) of the ungettered films increased as a function of deposition temperature until 600 °C. Similar behavior was observed previously through annealing, which suggests much of the increase in both cases is related to improved structure.[22] The upper bound of $M_{20\ kOe}$ for bulk Gd is shown in Fig. 5 as well as the upper bound expected due to suppression of the magnetization at the interface of the Gd with the Ta. For the latter, we refer to polarized neutron reflectometry data that enabled us to measure the depth profile of the magnetization in the Gd in a thin film heterostructure with the same thickness and a similar paramagnetic metal that is also immiscible with Gd.[23] $M_{20\ kOe}$ increases toward these bounds with deposition temperature, but that approach is made more readily for the gettered samples. Oxide incorporation clearly has a negative impact on the magnetization, though that can apparently be overcome, to some extent, with temperature. The drop in $M_{20\ kOe}$ at 600 °C shows that sample had become a purely diamagnetic oxide (see Fig. 1). Figure 6 shows $-\Delta S$ as a function of temperature for the ungettered and gettered samples for a field change of 1 T. From Fig. 6, the maximum of the $-\Delta S$ curves for the ungettered films increased with deposition temperature and the magnetic ordering temperature (T_c) shifted to higher temperatures. The maximum $-\Delta S$ peak occurred for T_{depo} of 450 °C and had a value of 1.026 J/kg K. Figure 7 shows the $-\Delta S_{max}$, FWHM, and the RCP as a function of deposition temperature. In the ungettered films, $-\Delta S_{max}$ increases with increasing T_{depo}. The FWHM of the $-\Delta S$ curve remained relatively constant with respect to deposition temperature, and the

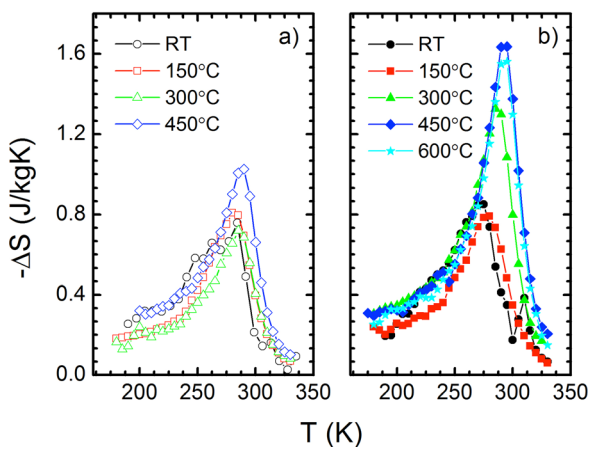

FIG. 6. (Color online) $-\Delta S$ vs temperature for (a) the ungettered and (b) the gettered samples for $\Delta H = 1$ T. The $-\Delta S$ peak increased with increasing deposition temperature and shifted to higher temperatures toward the T_c of bulk Gd (293 K). In the ungettered films, T_c ranged from 284 K for T_{depo} of room temperature to 290 K for T_{depo} of 450 °C. In the gettered films, T_c ranged from 275 K for T_{depo} of room temperature to 295 K for T_{depo} of 600 °C.

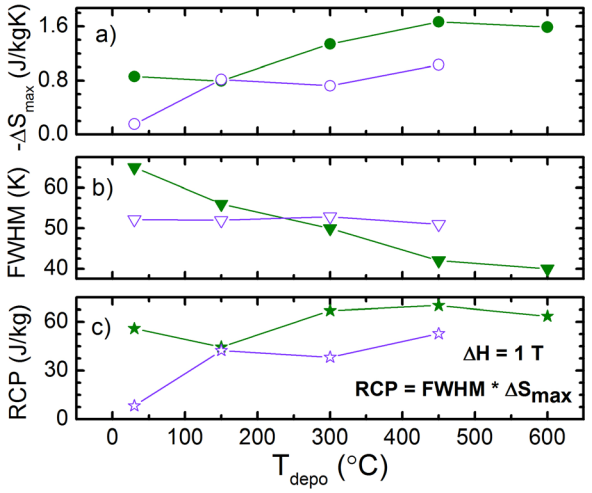

FIG. 7. (Color online) (a) $-\Delta S_{max}$, (b) FWHM, and (c) RCP as a function of deposition temperature for the ungettered (purple, open symbols) and the gettered (green, closed symbols) films.

RCP increased as a function of T_{depo} due to the increase in $-\Delta S_{max}$.

According to Fig. 5, the $M_{20\ kOe}$ values of the gettered films generally increased with T_{depo}, which is expected from previous work.[22] The increase in $M_{20\ kOe}$ approaches $M_{20\ kOe}$ for thin film Gd (137 emu/g)[23] but is still less than $M_{20\ kOe}$ for bulk Gd (162 emu/g). The maximum of the $-\Delta S$ curves and T_c increased with T_{depo}, with the exception of 600 °C (see Fig. 6). This decrease in $-\Delta S_{max}$ is apparent in Fig. 7 and was due to the increased presence of oxide phases. The FWHM decreased and the RCP increased as a function of T_{depo}. The drop off in the $-\Delta S_{max}$ is also reflected in the RCP where a similar drop off is apparent.

The $M_{20\,kOe}$ of the gettered films was larger than the ungettered films. The overall suppression of the $M_{20\ kOe}$ of the ungettered films was due to the increasing presence of Gd_2O_3 phase (see Fig. 2), which was diamagnetic as determined by magnetometry measurements of the ungettered film grown at 600 °C. The films grown at 150 °C had similar $M_{20\ kOe}$ values, 57.03 emu/g for ungettered and 59.61 emu/g for gettered. For both the ungettered and gettered films, there was an increase in T_{peak} with increasing T_{depo} toward the bulk T_c for Gd (293 K). This was likely due to structural order increasing with T_{depo}. Overall the magnitude of the $-\Delta S_{max}$ was larger in the gettered set with respect to the ungettered set. The ungettered film grown at 450 °C had a $-\Delta S_{max}$ value that was half of the value measured for bulk Gd ($-\Delta$Smax was measured to be 2.048 J/kg K for $\Delta H = 1$ T from a chip of bulk Gd). The gettered film grown at the same temperature had a $-\Delta S_{max}$ value that was approximately 80% of the $-\Delta S_{max}$ for bulk Gd. The RCP for the ungettered film grown at 450 °C was 52.83 J/kg, which was 65% of the RCP for bulk Gd (80.69 J/kg). For the gettered film grown at the same temperature, the RCP was 70.14 J/kg, which was 87% of the value for bulk Gd. The RCP value for the gettered film was 33% higher than the ungettered film grown at 450 °C. It is clear from these data that gettering improved the magnetic properties of Gd thin films.

IV. CONCLUSION

Deposition at elevated temperatures and gettering the film growth chamber are useful methods by which the MCE properties of Gd thin films can be enhanced. Gettering improves the structural formation of the Gd (110) phase, while increasing the substrate temperature favors oxide formation. These oxide impurities have negative impacts on the MCE properties as shown in the sample grown at 600 °C without gettering. This sample was purely GdO (111) and diamagnetic. Deposition at elevated temperatures can increase the roughness of the gettered films by introducing another phase of Gd as shown in the XRD data for the gettered films deposited at 450 and 600 °C. The occurrence of both Gd phases appears to increase the surface roughness of these films. Gettering before film growth increased the RCP power values by as much as 33% for the films grown at 450 °C. The enhancement of the magnetic properties of the Gd films is clearly shown in the RCP value for the gettered film grown at 450 °C, which was 87% of the value for bulk Gd.

ACKNOWLEDGMENTS

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[1]J. K. A. Gschneidner and V. K. Pecharsky, Annu. Rev. Mater. Sci. **30**, 387 (2000).
[2]E. Warburg, Ann. Phys. Chem. **13**, 141 (1881).
[3]W. F. Giauque and D. P. MacDougall, Phys. Rev. **43**, 768 (1933).
[4]P. Debye, Ann. Phys. **81**, 1154 (1926).
[5]A. M. Tishin and Y. I. Spichkin, *The Magnetocaloric Effect and Its Applications* (Institute of Physics Publishing, Bristol, 2003).
[6]V. K. Pecharsky and K. A. Gschneidner, Jr., J. Magn. Magn. Mater. **200**, 44 (1999).
[7]E. Bruck, J. Phys. D: Appl. Phys. **38**, R381 (2005).
[8]M. H. Phan and S. C. Yu, J. Magn. Magn. Mater. **308**, 325 (2007).
[9]T. Samanta, I. Das, and S. Banerjee, Appl. Phys. Lett. **91**, 082511 (2007).
[10]F. Hu, B. Shen, J. Sun, and G. Wu, Phys. Rev. B **64**, 132412 (2001).
[11]H. Wada and Y. Tanabe, Appl. Phys. Lett. **79**, 3302 (2001).
[12]S. Fujieda, A. Fujita, and K. Fukamichi, Appl. Phys. Lett. **81**, 1276 (2002).
[13]L. Li, K. Nishimura, and H. Yamane, Appl. Phys. Lett. **94**, 102509 (2009).
[14]V. Pecharsky and K. Gschneidner, Phys. Rev. Let. **78**, 4494 (1997).
[15]C. W. Miller, D. V. Williams, N. S. Bingham, and H. Srikanth, J. Appl. Phys. **107**, 09A903 (2010).
[16]S. Gorsse, B. Chevalier, and G. Orveillon, Appl. Phys. Lett. **92**, 122501 (2008).
[17]M. H. Phan, S. Chandra, N. S. Bingham, H. Srikanth, C. L. Zhang, S. W. Cheong, T. D. Hoang, and H. D., Chinh. Appl. Phys. Lett. **97**, 242506 (2010).
[18]S. Y. Dan'kov, A. M. Tishin, V. K. Pecharsky, and K. A. Gschneidner, Phys. Rev. B **57**, 3478 (1998).
[19]C. Zimm, A. Jastrab, A. Sternberg, V. Pecharsky, K. A. Gschneidner, Jr., M. Osborne, and I. Anderson, Adv. Cryog. Eng. **43**, 1759 (1998).
[20]J. K. A. Gschneidner, V. K. Pecharsky, and A. O. Tsokol, Rep. Prog. Phys. **68**, 1479 (2005).
[21]L. Gan, R. D. Gomez, C. J. Powell, R. D. McMichael, P. J. Chen, and J. W. F. Eglehoff, J. Appl. Phys. **93**, 8731 (2003).
[22]D. V. Williams, Jr., "Characterization of the structural and magnetic properties of Gd thin films," Master's thesis (University of South Florida, Tampa, FL, 2012).
[23]B. J. Kirby, J. W. Lau, D. V. Williams, C. A. Bauer, and C. W. Miller, J. Appl. Phys. **109**, 063905 (2011).