Calorimetry of epitaxial thin films

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Thin film growth allows for the manipulation of material on the nanoscale, making possible the creation of metastable phases not seen in the bulk. Heat capacity provides a direct way of measuring thermodynamic properties of these new materials, but traditional bulk calorimetric techniques are inappropriate for such a small amount of material. Microcalorimetry and nanocalorimetry techniques exist for the measurements of thin films but rely on an amorphous membrane platform, limiting the types of films which can be measured. In the current work, ion-beam-assisted deposition is used to provide a biaxially oriented MgO template on a suspended membrane microcalorimeter in order to measure the specific heat of epitaxial thin films. Synchrotron x-ray diffraction showed the biaxial order of the MgO template. X-ray diffraction was also used to prove the high quality of epitaxy of a film grown onto this MgO template. The contribution of the MgO layer to the total heat capacity was measured to be just 6.5% of the total addenda contribution. The heat capacity of a Fe₄₀Rh₅₁ film grown epitaxially onto the device was measured, comparing favorably to literature data on bulk crystals. This shows the viability of the MgO/SiNₓ-membrane-based microcalorimeter as a way of measuring the thermodynamic properties of epitaxial thin films. © 2011 American Institute of Physics. [doi:10.1063/1.3554440]

I. INTRODUCTION

Calorimetry is a useful technique for observing a host of physical phenomena from the thermodynamics of a phase transition or a novel two-state system to electron and phonon densities of states or the symmetry of high-TC superconductors. As thin film technology has emerged as a way to manipulate materials on the microscopic scale, producing novel and often useful properties, it has become even more crucial to understand the fundamental properties of these materials and how these novel properties emerge. However, traditional bulk calorimetric techniques have far too large an addenda to be used on thin films.¹

Over the past 15 years, there has been an emergence of novel “thin film” calorimeters fabricated with MEMS processes.²⁻⁹ These microcalorimeters use a thin membrane to reduce the background addenda and thermal link to an appropriate level for thin films. A common technique is to suspend the sample of interest on a thin membrane (most commonly amorphous silicon nitride, a-SiNₓ), which acts both as support and a weak thermal link to the sample stage. While the low thermal conductivity of the membrane provides for good thermal isolation, its amorphous structure does not provide a platform to grow high-quality ordered thin film structures. Thus far, the calorimeters have primarily been used for measuring small bulk samples (<100 µg) and amorphous or polycrystalline films. However, this excludes many of the novel thin film systems of current interest such as dilute magnetic semiconductors or high-TC superconductors.

To overcome this obstacle, we turn to the high-TC superconductivity community for an answer. They use ion-beam-assisted deposition (IBAD) to grow biaxially textured MgO(001) onto long metallic tapes, onto which high-quality YBa₂Cu₃O₇−δ films are grown as a way of scaling up ordered high-TC superconductors for industrial applications.¹⁰,¹¹ We used a similar IBAD technique to grow biaxially oriented MgO onto our a-SiNₓ-based microcalorimeters, providing a template for the growth of epitaxial thin films. A Fe–Rh film epitaxially grown onto this device has been characterized and measured as a proof of functionality.

II. EXPERIMENTAL SETUP

A. Calorimeter fabrication

To create these microcalorimeters, we start from a (001)-oriented double-polished Si wafer. On this, we deposit via chemical vapor deposition (CVD) a high-temperature “wet” (steam + O₂) silicon oxide, yielding a smooth buffer layer of 300 nm; this oxide layer reduces capacitive links between thermometers and heaters. A 200 nm low-stress (off-stoichiometry) silicon nitride layer is then deposited via low-pressure CVD to provide the sample platform and act as our weakly thermally conductive link, as described above. We then use DC magnetron sputtering to deposit Pt electrical leads, thermometers, and the sample heater. The Si is then etched away in the central area, leaving a Si frame around the outside and a thin a-SiNₓ membrane with heaters and thermometers in the center. The next step in processing of our devices is the sputtering of a-Nb₅Si₁₋ₓ (x ≈ 0.1) for use.

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as sensitive low-temperature thermometers. A more detailed description of the fabrication process may be found in earlier work.3, 12

B. IBAD MgO growth

The IBAD MgO layer was deposited onto the back side of the device (i.e., the side of the membrane opposite the thermometer and heaters). All depositions were conducted in a high vacuum chamber with a base pressure less than $5 \times 10^{-8}$ torr. A 5 nm nucleation layer of polycrystalline Si$_3$N$_4$ was first deposited on the membrane surface via electron beam deposition at room temperature. The IBAD MgO layer was then deposited with concurrent 750 eV Ar$^+$ and e-beam evaporated MgO fluxes. A two-grid collimated Kaufman ion source at an incidence angle of 45° relative to the substrate normal provided the Ar$^+$ ion flux. The ion-to-atom ratio was kept constant at ≈0.8. Deposition was monitored throughout the process in situ using reflection high-energy electron diffraction. After a 10 nm IBAD MgO layer was deposited, the substrate temperature was raised to 300°C, and a 15 nm homoepitaxial MgO layer was deposited via e-beam. This final layer acts to “heal” the surface and create a better quality substrate.10

Because the MgO layer is grown on the backside of the device, the silicon frame acts to shadow a small fraction of the surface from the Ar$^+$ ion beam, resulting in a small fraction of the outer membrane area with a slightly thicker polycrystalline MgO region (a 150 μm-wide band along the 0.5 cm length of the window). However, because this is on the outer edge of the membrane adjacent to the Si frame, it does not affect areas of the membrane where any subsequent film will be deposited, nor does it significantly alter the thermal contours or thermodynamic properties of our device.13

C. Relaxation calorimetry

Once the film of interest (e.g., Fe$_{40}$Rh$_{51}$) has been deposited onto the IBAD MgO template, we thermally evaporate a 200 nm Cu or Au film on top of it to create an isothermal sample area.13 Because this sample area is weakly linked to the Si frame, we employ the semiadiabatic relaxation method of calorimetry.

The relaxation technique first consists of stabilizing the temperature of the entire calorimeter and its environment at a desired base temperature $T_0$. Next, a constant power $P$ is applied to the sample via the Pt heater, allowing it to reach a steady state where the power in is equal to the heat flow out. The equilibrium temperature difference $\Delta T$, measured by one of the three thermometers in the central sample area (depending on temperature range), yields the value of the thermal conductance, $\kappa = P/\Delta T$, of the device. After obtaining $\kappa$, we turn off the power to the sample heater and monitor the temperature decay. In the limit $\Delta T \ll T_0$, this decay is exponential with a single time constant, $\tau$, assuming a good thermal link between the sample and the thermometers, with $\tau = C/\kappa$ where $C$ is the total heat capacity. This heat capacity $C$ includes that of the sample and addenda (membrane, thermometers, and heater). The addenda is separately measured (without sample) and subtracted to obtain the heat capacity of the sample. Further description of our methodology as well as determination of membrane and lead contributions and systematic absolute errors is available elsewhere.3, 13

III. RESULTS

We now turn to the analysis of key parameters of the device: (1) crystalline quality of the IBAD MgO template; (2) crystalline quality of a film grown on this template; (3) the contribution of the IBAD MgO layer to the addenda heat capacity; and (4) representative specific heat data of an epitaxial film grown on these devices.

A. X-ray diffraction data

To characterize the quality of the IBAD MgO layer, we used x-ray diffraction measurements at the Stanford Synchrotron Radiation Lightsource, carried out at beamlines 7-2 and 10-2 with 12 keV x-ray radiation. All measurements were carried out on conventional substrates (a-SiO$_x$ on Si) to act as a surrogate for the devices because they have been shown to have comparable surface roughness to the membrane.14 Structural characterization was performed by grazing incidence x-ray diffraction to reduce scattering from the substrate. We then performed $hk$ reciprocal space maps around several lattice points to quantify the crystallinity of the IBAD MgO film (Fig. 1). The off-center peaks in the $hk$ planes indicate a small out-of-plane tilt ($\leq 5^\circ$) and strain in the MgO. Combining these data with the $I$ scans, we see that the MgO is biaxially textured, as desired, with a small tetragonal distortion along the beam in-plane, leading to two in-plane lattice constants, $a = 4.228$ Å along [020] and $b = 4.202$ Å along [200] (for reference, the ion beam was directed in the...
FIG. 2. (Color online) (a) Out-of-plane and (b) in-plane x-ray diffraction measurements of a 200 nm Fe$_{49}$Rh$_{51}$ film grown on IBAD MgO on an a-SiO$_x$/Si substrate. Note the four-fold in-plane symmetry indicating epitaxy.

[202] direction during growth). The out-of-plane lattice constant matches the bulk value, $c = 4.212$ Å. This in-plane tetragonal strain is the source of the strain fields seen in IBAD MgO nanocalorimeters, which have a 30-nm-thick membrane (the strain will need to be addressed in order to use this technique for nanocalorimetry).\(^\text{16}\)

We then sputtered Fe$_{49}$Rh$_{51}$ onto the IBAD MgO substrate and devices and onto a MgO(001) substrate for comparison. Fe–Rh alloys form the CsCl structure at this composition\(^\text{17}\) and undergo a metamagnetic antiferromagnetic-to-ferromagnetic phase transition that is very sensitive to structural disorder.\(^\text{18}\) The Fe–Rh films grow [001] out-of-plane, but because the lattice constant is approximately $\sqrt{2}$ smaller, the films are rotated 45° in-plane relative to the MgO. To characterize the ordering of the films grown on IBAD MgO, we measured out-of-plane x-ray diffraction along the [001] axis and in-plane diffraction at a 45° tilt to examine the (011) peaks. A $\theta$–2$\theta$ scan at that tilt was used to obtain the location of the (011) peak and, thus, extract the lattice parameters for the films. Figure 2 shows the out-of-plane and in-plane x-ray diffraction data taken on the film grown on IBAD MgO. In-plane data show the four-fold symmetry expected for an epitaxial film with the body-centered-cubic structure, while out-of-plane XRD shows the clear, highly ordered CsCl superlattice peaks. The IBAD MgO substrate shows orthorhombic structure ($a \neq b \neq c$), which could lead to monoclinic ordering in the Fe$_{49}$Rh$_{51}$ film—however, within the resolution of the detector, four (011) peaks were observed exactly 90° apart and showed no asymmetry, indicating a tetragonal structure ($a = b \neq c$).

The lattice constants for the films grown on the MgO and IBAD MgO films show a small difference in film structure—the films grown on MgO exhibit compressive strain, with $a = b = 2.980$ Å and $c = 3.004$ Å, while the films grown on IBAD MgO have $a = b = 3.005$ Å and $c = 2.959$ Å (compare to $a = b = c = 2.987$ Å for the bulk). This is due to the different in-plane lattice constant for IBAD MgO, as noted above. In the films grown on IBAD MgO, this change in strain leads to a more bulklike behavior, showing exactly the same critical temperature as the bulk and one much lower than that of the compressively stressed films grown on MgO ($T_{\text{crit}} = 330$ K, as compared to $328 \pm 2$ K for a bulk crystal\(^\text{19}\) and 380 K for the film grown on MgO). The IBAD MgO, thus, forms a useful substrate.

B. Calorimetry data

We now characterize the effect of the IBAD MgO layer on our measurement technique. Figure 3(b) shows the additional heat capacity of the device. At room temperature, there is a net $\sim 700$ nJ/K increase from the device without the MgO layer, or only about 6.5% of the total addenda measurement.

FIG. 3. (Color online) The black squares are the specific heat contribution of the IBAD MgO layer. Shading represents the average error. A representative error bar is shown at 300 K. The large scatter in the data is due to the fact that the IBAD is a mere 6.5% of the total addenda, as indicated in inset (b), where the total heat capacities are shown for a device with (black squares) and without (blue open circles) the IBAD layer. The red curve through the data is the value of bulk MgO (Ref. 20). Inset (a) is the low-temperature IBAD MgO data shown as $C/T$ vs $T^2$, with the red line being a fit to the data yielding a Debye temperature of 440 ± 130 K, where again we note the large uncertainty is because the IBAD MgO layer represents less than 6% of the total measured signal.
At low temperatures, the specific heat of the MgO layer falls off as $T^3$, much faster than the $C \propto T$ contribution of both the a-SiN$_x$ layer$^{12}$ and the metallic thermal conduction layer; so this fraction decreases at low temperature.

Figure 3 shows that the contribution of the IBAD MgO layer can be modeled very well by bulk MgO. Though this contribution is small [as shown in Fig. 3(b)], it could be further reduced by a factor of 2 by eliminating the MgO outside the sample area [we note that the fractional contribution from the MgO outside the sample area is only 24% (Ref. 13)]. Though it matches well to the bulk value at high temperature, the low-temperature data [Fig. 3(a)] indicate a softening of phonons with a lower Debye temperature, 440 ± 8 K.21 We suspect this has to do with either the strain in the film mentioned earlier or the bombardment process itself which is known to create damage and lower the Debye temperature in thin films.22

Given this near-negligible heat capacity contribution of IBAD MgO to the device, we next measured the specific heat of a Fe$_{49}$Rh$_{51}$ film grown epitaxially onto an IBAD MgO microcalorimeter, shown in Fig. 4. The data match that of the bulk well. There is a very good agreement with the results of Richardson et al. from 100 to 300 K,19 and at low temperatures, the results of the Sommerfeld coefficient, $\gamma = 22 \pm 2 \mu \text{J/g/K}^2$, is well within the range of data seen in the literature ($\gamma = 16 - 24 \mu \text{J/g/K}^2$).23,24 However, we do observe a softening in the lattice, evidenced by a lower $\Theta_D = 340 \pm 13$ K as compared to $\Theta_D = 390 - 410$ K. We attribute this difference to the increased mosaicity of the Fe–Rh film grown on the IBAD MgO as compared to the bulk, as evidenced by the larger FWHM of the XRD peaks.

IV. CONCLUSIONS

In order to measure the specific heat of epitaxial thin films, we have used ion-beam-assisted deposition to grow a biaxially oriented MgO substrate on the amorphous SiN$_x$ membrane of our thin film calorimeters. X-ray diffraction confirmed the biaxial nature of the IBAD MgO substrate and the highly ordered epitaxial structure of the subsequent Fe$_{49}$Rh$_{51}$ film grown on that substrate. The heat capacity of this thin MgO layer compares well with the bulk and adds only a small ($\sim 6\%$) contribution to the addenda of our microcalorimeters. We used these new calorimeters to measure the specific heat of an epitaxial Fe$_{49}$Rh$_{51}$ film and showed that it compares well to bulk sample values in the literature.

The successful fabrication of these new devices offers a wealth of possibilities for new thermodynamic studies of high-quality nanostructures such as multiiferroics, dilute magnetic semiconductors, high-$T_c$ superconductors, and a range of other thin films that can be grown epitaxially onto a MgO substrate.

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