Total Energy CMR Production

Stephan Friedrich  
Author  
Signature  
Date 09/25/08

Richard Bionta  
XTOD Manager  
Signature  
Date 10/8/08

Peter Stefan  
XTOD Physics Liaison  
Signature  
Date 2008/9/25

John Arthur  
Photon Systems Manager  
Signature  
Date 10-9-08

Darren Marsh  
Quality Assurance Manager  
Signature  
Date 9/29/08

Summary:  
This outlines the production steps performed at Towson University to fabricate the temperature sensors for the Total Energy Measurement System.

Change History Log

<table>
<thead>
<tr>
<th>Rev Number</th>
<th>Revision Date</th>
<th>Sections Affected</th>
<th>Description of Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>000</td>
<td>2008/9/10</td>
<td>All</td>
<td>Initial Version</td>
</tr>
</tbody>
</table>
Disclaimer

This document was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor Lawrence Livermore National Security, LLC, nor any of their employees makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or Lawrence Livermore National Security, LLC. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or Lawrence Livermore National Security, LLC, and shall not be used for advertising or product endorsement purposes.

Auspices Statements

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. This work was performed in support of the LCLS project at SLAC.
Executive Summary:

The following outlines the optimized pulsed laser deposition (PLD) procedure used to prepare Nd\textsubscript{0.67}Sr\textsubscript{0.33}MnO\textsubscript{3} (NSMO) temperature sensors at Towson University (Prof. Rajeswari Kolagani) for the LCLS XTOD Total Energy Monitor. The samples have a sharp metal/insulator transition at T ~ 200 K and are optimized for operation at T ~ 180 K, where their sensitivity is the highest. These samples are epitaxial multilayer structures of Si/YSZ/CeO/NSMO, where these abbreviations are defined in the following table:

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Material</th>
<th>Approximate Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>YSZ</td>
<td>Y:ZrO\textsubscript{2} (8 mole % Y\textsubscript{2}O\textsubscript{3} in ZrO\textsubscript{2})</td>
<td>Initial Bottom Layer: 10 nm&lt;br&gt;Second over-Layer: 240 nm</td>
</tr>
<tr>
<td>CeO</td>
<td>CeO\textsubscript{2}</td>
<td>22.5 nm</td>
</tr>
<tr>
<td>BTO</td>
<td>Bi\textsubscript{4}Ti\textsubscript{3}O\textsubscript{12}</td>
<td>17 nm</td>
</tr>
<tr>
<td>NSMO</td>
<td>Nd\textsubscript{0.67}Sr\textsubscript{0.33}MnO\textsubscript{3}</td>
<td>160 nm</td>
</tr>
</tbody>
</table>

Table 1: Details of the Multilayer Structure

In this heterostructure, YSZ serves as a buffer layer to prevent deleterious chemical reactions, and also serves to de-oxygenate the amorphous SiO\textsubscript{2} surface layer to generate a crystalline template for epitaxy. CeO and BTO serve as template layers to minimize the effects of thermal and lattice mismatch strains, respectively. More details on the buffer and template layer scheme are included in the attached manuscript accepted for publication in Sensor Letters (G. Yong et al., 2008)
Pulsed Laser Deposition

Figure 1: Schematic Drawing of the Pulsed Laser Deposition (PLD) Chamber

The multilayers were grown by Pulsed Laser Deposition (PLD) on (100)-oriented Silicon substrates (provided by LLNL) using commercially available bulk ceramic targets of the appropriate material. Pulsed Laser Deposition (PLD) involves ‘ablation’ of a bulk ceramic disk (target) of the desired composition using a high power pulsed UV Laser. The ablated material is deposited on a substrate held at a high temperature that is optimized for the specific material being grown. The deposition ambient atmosphere is usually high purity oxygen gas, maintained at a few hundred milliTorr pressure. Details of the deposition ambient are also material-specific. A Pulsed Laser Deposition System with an automated target carousel (manufactured by Neocera Inc.) was used together with a KrF excimer laser (COMPEX 205, manufactured by Coherent) with a wavelength of 248 nm and pulse duration of 25 ns. The pulse energy is varied in conjunction with the spot size on the target to obtain the optimum fluence (energy density). The target is rotated and rastered during the deposition to avoid damage of the target surface by the high-power laser pulses. Figure 1 shows a schematic of the Pulsed Laser Deposition process.

Several parameters play a crucial role in determining the properties of thin films grown by PLD such as:

- Laser energy density (determined by the pulse energy and spot size)
- Substrate temperature
- Partial pressure of the ambient gas during growth
- Oxygen partial pressure during cool down
- Temperature ramp rates during the heating and cooling steps

These parameters were optimized to grow Nd$_{0.67}$Sr$_{0.33}$MnO$_3$ (NSMO) films to be used as sensors in the Total Energy Monitor at the LCLS for operation at a temperature $T \sim 180$ K.
Table 2: PLD Parameters for the multilayer scheme

<table>
<thead>
<tr>
<th>Material</th>
<th>Growth temperature (°C)</th>
<th>Pre-ablation conditions</th>
<th>Laser Pulse Energy &amp; Pulse Repetition Rate</th>
<th>Ambient gas pressure during growth and/or cool down</th>
<th>Heating and cooling rates</th>
</tr>
</thead>
<tbody>
<tr>
<td>YSZ (Initial layer, ~10 nm)</td>
<td>780</td>
<td>Vacuum; 1500 pulses of 580 mJ at 10 Hz</td>
<td>580 mJ, 10 Hz (500 pulses)</td>
<td>$2 \times 10^{-6}$ Torr (residual air)</td>
<td>Heated to 780 °C at 20 °C/min</td>
</tr>
<tr>
<td>YSZ (Second layer, ~240 nm)</td>
<td>780</td>
<td>-</td>
<td>580 mJ, 10 Hz (18000 pulses)</td>
<td>$4 \times 10^{-4}$ Torr oxygen (O₂)</td>
<td>Cooled to 750 °C at 3 °C/min</td>
</tr>
<tr>
<td>CeO (~22.5 nm)</td>
<td>750</td>
<td>580 mJ 10 Hz (1500 pulses)</td>
<td>580 mJ, 10 Hz (1500 pulses)</td>
<td>$1.5 \times 10^{-3}$ Torr oxygen</td>
<td>Cooled to 650 °C at 3 °C/min</td>
</tr>
<tr>
<td>BTO (~17 nm)</td>
<td>650</td>
<td>580 mJ 10 Hz (1500 pulses)</td>
<td>580 mJ, 10 Hz (1500 pulses)</td>
<td>400 mTorr O₂</td>
<td>Heated to 790 °C at 5 °C/min</td>
</tr>
<tr>
<td>NSMO (~160 nm)</td>
<td>790</td>
<td>580 mJ 10 Hz (1500 pulses)</td>
<td>580 mJ, 10 Hz (8000 pulses)</td>
<td>400 mTorr O₂ (growth) ~500 Torr O₂ (cooling)</td>
<td>Cooled to room temperature at 1 °C/min</td>
</tr>
</tbody>
</table>

Film Growth Procedure

A typical successful deposition run involves the following procedure:

1. The target surfaces are sanded and targets are fixed on the target carousel after blow drying using a nitrogen gun.

2. The substrates are sequentially cleaned using trichloroethylene, acetone and methanol (in that order, for 5 minutes each) in an ultrasonic cleaner and dried using a nitrogen blow gun.

3. The substrates are pasted onto the heater block of the PLD chamber using a Conducting Ag paint (Ted Pella Inc. Leitsilber 200; product # 16035). To do this, a small amount of Ag paint is brushed onto the heater plate to cover an area almost equal to the substrate size. The substrate is then gently (and quickly) dropped onto the Ag paint. Corners of the substrate are gently pressed down to squeeze out any trapped air bubbles. Afterwards, the substrate is heated slowly at ~2 °C/minute up to 100 °C, and at 10 °C/minute from 100 °C to 200 °C. The heater flange is replaced in the vacuum chamber.

4. The quartz window at the laser beam entry port is cleaned using diamond paste (1 micron in suspension, Buehler MetaDi Supreme diamond polishing compound; Product # 40-630) followed by rinsing in methanol. This step is essential if the previous run had a YSZ deposition, since the layer that is coated onto the window cuts down laser energy due to
absorption and reflection. [If the previous deposition did not include YSZ, diamond paste cleaning is not essential. Cleaning with dilute (2%) HCl will suffice to remove other coatings].

5. The chamber is pumped down to the base pressure, at least below $\sim 5 \times 10^{-6}$ Torr.

6. The substrate is heated to 780 °C, which is the deposition temperature of the first layer (YSZ).

7. With the substrate shutter in place to block the substrate, the target is ‘pre-ablated’ with 1500 laser pulses at a repetition rate of 10 Hz. [The pre-ablation step serves to remove the first few layers of the target to avoid possible contamination].

8. The substrate shutter is opened and the initial layer of YSZ is deposited with 500 pulses at 10 Hz rep rate. The pulse energy during this deposition is 580 mJ. Note that this number actually depends on the details of the laser optics and the focused spot size on the target, which can vary between deposition systems. The corresponding laser fluence is approximately 1.5 to 2 J/cm² [This initial layer of YSZ serves to de-oxygenate the native SiO₂ layer on the substrate].

9. The turbo pump is switched to speed control mode, the oxygen inlet valves are opened and a pressure of $4 \times 10^{-4}$ Torr of oxygen is stabilized by adjusting both the gas flow control valve and the turbo pump speed.

10. A second YSZ layer is deposited (18000 pulses at 20 Hz) at the same laser fluence as in (8).

11. Following YSZ deposition, the substrate temperature is ramped down at 3 °C/min and stabilized at 750 °C for deposition of the CeO layer. The O₂ pressure is stabilized at 400 mTorr.

12. With the substrate shutter in place, the CeO target is pre-ablated (1500 pulses at 10 Hz).

13. 750 pulses of CeO₂ are deposited at a repetition rate of 10 Hz.

14. The temperature is ramped down at 3 °C/min and stabilized at 650 °C for the deposition of the BTO layer.

15. With the substrate shutter in place, the BTO target is pre-ablated (1500 pulses at 10 Hz).

16. 750 pulses of BTO are deposited at 10 Hz.

17. The temperature is ramped up at 5 °C/min and stabilized at 790 °C for the deposition of the NSMO layer.

18. With the substrate shutter in place, the NSMO target is pre-ablated (1500 pulses at 10 Hz).

19. 8000 pulses of NSMO are deposited at 10 Hz.

20. The gate valve to the turbo pump is closed, and the pump is turned off. The oxygen inlet valve is opened to let in ~500 Torr of oxygen into the chamber.

21. The substrate temperature is ramped down to room temperature at 1 °C/min.

22. When the heater block has cooled down to room temperature (or below 60 °C), the chamber is vented (with oxygen or air) and the sample is removed from the heater block.

23. The 2-probe resistance is measured with a digital multimeter as a quick diagnostic check.

24. The sample is characterized by 4-circle X-ray diffraction (4-probe resistance and TCR measurements are also done for select samples).
Details of the Samples Delivered:

Properties of the 8 final multilayer samples delivered are summarized in the following table. In addition, 7 samples with properties within the required specification and over 35 samples produced during the process optimization stage were also delivered prior to the delivery of the final samples.

The typical temperature dependence of the sample resistance and the sensitivity, given by the temperature coefficient of resistance $\text{TCR} \equiv 1/R \times \partial R/\partial T$, are shown in figure 2. Figure 3 shows a typical X-ray 2$\Theta$-$\Theta$ scan of a high-quality sample. X-ray $\varphi$-scans indicating epitaxial alignment of the different layers are shown in figure 4.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Resistance</th>
<th>X-ray Diffraction</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>NSMOA119</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BTO/CeO$_2$/YSZ/floatzone pSi</td>
<td>2 probe: 3.3 – 5 kΩ</td>
<td>High intensity peaks</td>
</tr>
<tr>
<td></td>
<td>4 probe: $T_{\text{peak}} = 218$ K</td>
<td>NSMO(002) FWHM$_{\text{rock}}$ =</td>
</tr>
<tr>
<td></td>
<td>$\text{TCR}_{\text{max}} = 13%$</td>
<td>0.55°</td>
</tr>
<tr>
<td></td>
<td>$R_{\text{peak}} = 2950$ Ω</td>
<td></td>
</tr>
<tr>
<td><strong>NSMOA122</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BTO/CeO$_2$/YSZ/floatzone pSi</td>
<td>2 probe: 3 – 3.8 kΩ</td>
<td>High intensity peaks</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NSMO(002) FWHM$_{\text{rock}}$ =</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.75°</td>
</tr>
<tr>
<td><strong>NSMOA124</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BTO/CeO$_2$/YSZ/floatzone pSi</td>
<td>2 probe: 2.7 – 3.7 kΩ</td>
<td>High intensity peaks</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NSMO(002) FWHM$_{\text{rock}}$ =</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.59°</td>
</tr>
<tr>
<td><strong>NSMOA125</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BTO/CeO$_2$/YSZ/floatzone pSi</td>
<td>2 probe: 3 – 3.9 kΩ</td>
<td>High intensity peaks</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NSMO(002) FWHM$_{\text{rock}}$ =</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.61°</td>
</tr>
<tr>
<td><strong>NSMOA126</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BTO/CeO$_2$/YSZ/low $\rho$ nSi</td>
<td>2 probe: 3.5 kΩ</td>
<td>High intensity peaks</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NSMO(002) FWHM$_{\text{rock}}$ =</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.61°</td>
</tr>
<tr>
<td><strong>NSMOA128</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BTO/CeO$_2$/YSZ/low $\rho$ nSi</td>
<td>2 probe: 5 kΩ</td>
<td>High intensity peaks</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NSMO(002) FWHM$_{\text{rock}}$ =</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.79°</td>
</tr>
<tr>
<td><strong>NSMOA130</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BTO/CeO$_2$/YSZ/low $\rho$ nSi</td>
<td>2 probe: 5 kΩ</td>
<td>High intensity peaks</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NSMO(002) FWHM$_{\text{rock}}$ =</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.57°</td>
</tr>
<tr>
<td><strong>NSMOA133</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BTO/CeO$_2$/YSZ/low $\rho$ nSi</td>
<td>2 probe: 5 kΩ</td>
<td>High intensity peaks</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NSMO(002) FWHM$_{\text{rock}}$ =</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.84°</td>
</tr>
</tbody>
</table>
In addition, the following samples, sent in a prior shipment, are comparable in properties to the final set of 8 samples above:

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Resistance</th>
<th>X-ray Diffraction</th>
</tr>
</thead>
</table>
| **NSMOA112** BTO/CeO₂/YSZ/floatzone pSi | 2 probe: 3.3 – 4 kΩ  
4 probe: $T_{\text{peak}} = 178$ K  
TCR$_{\text{max}} = 6\%$  
$R_{\text{peak}} = 5400$ Ω  
Same as final recipe except may have started NSMOA deposition at 780°C instead of waiting until 790°C. | High intensity peaks  
NSMO(002) FWHM$_{\text{rock}} = 0.52°$ |
| **NSMOA113** BTO/CeO₂/YSZ/floatzone pSi | 2 probe: 5 – 7 kΩ  
4 probe: $T_{\text{peak}} = 205$ K  
TCR$_{\text{max}} = 11.5\%$  
$R_{\text{peak}} = 5625$ Ω  
Same as final recipe. Sample was made with no apparent mistakes; don’t know why resistance is a tad higher. | High intensity peaks  
NSMO(002) FWHM$_{\text{rock}} = 0.51°$ |
| **NSMOA115** BTO/CeO₂/YSZ/floatzone pSi | 2 probe: 4 – 5 kΩ  
4 probe: $T_{\text{peak}} = 217$ K  
TCR$_{\text{max}} = 12.7\%$  
$R_{\text{peak}} = 3060$ Ω  
Same as final recipe except mistake was made in the heating step 4) which seems to not have had any adverse effect. | High intensity peaks  
NSMO(002) FWHM$_{\text{rock}} = 0.52°$ |
Fig. 2: Resistance vs temperature for an optimized NSMO film

Fig. 3: 2Θ-Θ X-ray diffraction scan of an optimized NSMO film.
Fig. 4: X-ray diffraction $\phi$-scan, showing epitaxial alignment of the different layers in the multilayer structure NSMO[110] // BTO[100] // CeO2[100] // YSZ[100] // Si[100].
Colossal Magnetoresistive Manganite Based Fast Bolometric X-ray Sensors for Total Energy Measurements of Free Electron Lasers

Towson University, Department of Physics, Astronomy and Geosciences, Towson, MD 21252

Y. Liang
Motorola, Physical Science Research Laboratories, 7700 S. River Parkway Tempe, AZ 85284

O. B. Drury, S. P. Hau-Riege, C. Gardner, E. Ables, R. M. Bionta, S. Friedrich
Lawrence Livermore National Laboratory, 7000 East Ave., Livermore, CA 94550

*Corresponding author: Dr. Grace J. Yong, gyong@towson.edu
ABSTRACT

Bolometric detectors based on epitaxial thin films of rare earth perovskite manganites have been proposed as total energy monitors for X-ray pulses at the Linac Coherent Light Source free electron laser. We demonstrate such a detector scheme based on epitaxial thin films of the perovskite manganese oxide material Nd_{0.67}Sr_{0.33}MnO_3, grown by pulsed laser deposition on buffered silicon substrates. The substrate and sensor materials are chosen to meet the conflicting requirements of radiation hardness, sensitivity, speed and linearity over a dynamic range of three orders of magnitude. The key challenge in the material development is the integration of the sensor material with Si. Si is required to withstand the free electron laser pulse impact and to achieve a readout speed three orders of magnitude faster than conventional cryoradiometers for compatibility with the Linac Coherent Light Source pulse rate. We discuss sensor material development and the photoresponse of prototype devices. This Linac Coherent Light Source total energy monitor represents the first practical application of manganite materials as bolometric sensors.
INTRODUCTION

The next generation X-ray sources based on free electron lasers (FEL) will generate ultra-short coherent X-ray pulses through the process of self-amplified stimulated emission (SASE), whose peak brightness will exceed that of third generation synchrotrons by about ten orders of magnitude and their average brightness by three orders of magnitudes.\textsuperscript{1,2} They will enable wide-ranging novel science from atomic and chemical dynamics studies\textsuperscript{3} to single shot diffraction imaging.\textsuperscript{4} Among the different FEL sources currently being built, the Linac Coherent Light Source (LCLS) at the Stanford Linear Accelerator Center (SLAC) will be the first to extend operation to X-ray energies of 0.8 to 8 keV. LCLS is expected to produce $\sim 10^{12}$ X-rays per $\sim 200$ fs pulse with a repeat frequency of up to 120 Hz.\textsuperscript{5} Due to the statistical character of the SASE process, the pulse-to-pulse variations in photon number will be significant,\textsuperscript{2} and a crucial task will be to measure the energy of each pulse over the entire range of LCLS operating conditions.

Among the X-ray diagnostic instruments at LCLS, only a thermal detector is thought to be reliable, calibratable, and its response calculable in this new regime of ultra-short ultra-bright X-ray pulses where the response of other detectors will be non-linear or saturated, since most of the deposited laser energy will ultimately be converted into heat. A thermal total energy monitor can therefore be used during commissioning for X-ray FEL characterization and absolute calibration of other instruments, and during FEL operation for pulse intensity measurements at user end stations. For LCLS, this total energy monitor must be radiation hard in the X-ray band from 0.8 to 8 keV for energies up to $\sim 2$ mJ per pulse, must be sensitive down to the energy level of $\sim 1$ $\mu$J of the spontaneous undulator radiation, absolutely calibratable to $\leq 10\%$, and must be compatible with an operating frequency of at least 10 Hz for commissioning, preferably 120 Hz.
In this letter, we demonstrate a bolometric detector scheme based on a hole doped rare earth manganite (also known as colossal magneto resistive or ‘CMR’ manganite) sensor on a thin silicon substrate, for operation in the vicinity of its metal-insulator transition.\textsuperscript{6,7} CMR manganites are promising sensor materials, since their metal insulator transition temperature is determined by their cationic composition and can thus be tailored for a desired operating temperature. This tunability of operating temperatures makes manganites uniquely suited of the present application which demands flexibility in the operating temperature to allow the final detector design to accommodate possible unknown effects related to matter-energy interactions under unprecedented conditions. This is our foremost reason for choosing manganites over other potential thermal detector candidates. Given the fact that manganite materials have been a focus of applied materials research in the past decade, it is also noteworthy that the present detector represents the first practical application of manganite thin films as bolometric detectors.

Si has emerged as the absorber/substrate material of choice, since its low atomic number makes it radiation hard\textsuperscript{8}, its absorption characteristics allow calibration with conventional optical lasers, and lattice engineering schemes have been demonstrated for the epitaxial growth of CMR manganites such as $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ and $\text{La}_{0.67}\text{Ba}_{0.33}\text{MnO}_3$ on Si.\textsuperscript{9,10,11} A 500 µm Si chip will absorb >99.9% of the FEL energy at 8 keV while transmitting most of the spontaneous undulator radiation, and the subsequent increase in temperature can be measured as a change in resistance of the manganite sensor on the backside of the Si. The Si substrate also serves as the thermal link to the cold bath and sets the time constant of the pulse decay, and its high thermal diffusivity at low temperature makes it compatible with 120 Hz operation, .

For LCLS, sensor operation at lower temperatures is advantageous because of lower thermal noise and higher speed due to reduced phonon scattering. More specifically, 3D finite-
element simulations of the thermal response indicate that the signal in Si-based sensors operated
below $\leq 200$ K has decayed to $\leq 0.1\%$ after $\leq 100$ ms to allow operation at 10 Hz during
commissioning. Operation at the eventual LCLS frequency of 120 Hz is possible for sensors with
operating temperatures of $\leq 100$ K.\textsuperscript{12} However, many manganites with low metal-insulator
transition temperature exhibit two-phase (metallic and insulating) coexistence accompanied by
hysteresis in resistance vs. temperature and excess noise,\textsuperscript{13} which precludes use in detector
applications. For the desired temperature range, we identified Nd$_{1-x}$Sr$_x$MnO$_3$ (NSMO) with $x \approx
0.33$ as a suitable sensor material as it has no pronounced two-phase co-existence and negligible
hysteresis.\textsuperscript{6} High quality epitaxial films are required to maximize the temperature coefficient of
resistance $\text{TCR} = 1/R \partial R/\partial T$ and to minimize $1/f$ noise. We have therefore taken on the task to
develop epitaxial thin NSMO films on (001) oriented Si substrates using pulsed laser deposition
(PLD).

**EXPERIMENTAL METHODS**

The chemical reactivity of Si with manganites, lattice and thermal expansion mismatch,
and the easy formation of amorphous SiO$_2$ preclude the growth of high quality films directly on
bare Si and necessitate the use of buffer/template layers. Our initial efforts used Si substrates
with a 100 Å buffer of high-quality epitaxial SrTiO$_3$ (STO) deposited by molecular beam epitaxy
(MBE) at growth temperatures between $\sim 400$ and 550°C.\textsuperscript{14} NSMO layers were then grown
from a commercial bulk ceramic target by pulsed laser deposition (PLD), using a 248-nm KrF
pulsed excimer laser (COMPEX 205) with 25 ns pulse duration at a repetition rate of 5 Hz and a
fluence of $\sim 2$ J/cm$^2$. For a target-to-substrate distance of 8.5 cm this yielded typical deposition
rates of $\sim 0.3$ Å per pulse. NSMO growth was optimized at a substrate temperature of $\sim 780$ °C
with 400 mTorr of O₂ during deposition, and a post deposition cooling rate of 1 °C/min in ~400 Torr of O₂. Faster cooling rates encourage microcracks to develop in the NSMO due to differential thermal expansion coefficients (table 1). Structural analysis using a high resolution 4-circle X-ray diffractometer (Discover D8, Bruker AXS) shows that the films are phase-pure, epitaxial and in-plane aligned. The STO (002) out of plane peak gives a lattice parameter of 3.891 Å, close to the single crystal bulk value of 3.905 Å. The NSMO (002) pseudocubic out of plane peak gives a lattice parameter of 3.82 Å, which is smaller than the out-of-plane lattice constant 3.86 Å for bulk NSMO due to the lattice mismatch of STO and NSMO and the resulting tetragonal lattice distortion. Typical rocking angle widths for the STO and NSMO layers are 0.16° and 0.48° FWHM, respectively, indicating good crystallinity. The phi-scans show epitaxial in-plane alignment between the substrate and each of the different layers employed in the multilayer scheme. These NSMO films exhibit a metal-insulator transition around ~180 K and a maximum temperature coefficient of resistance TCR = 9.4 %/K at 143 K. The transition temperature is considerably suppressed and the peak resistivity is increased compared to strain-relaxed (thicker) NSMO films on LaAlO₃. This may be understood as due to the tensile strain from the lattice mismatch between NSMO and STO, which has been suggested to act as a Jahn-Teller type strain field, lifting the degeneracy of Mn³⁺ eg levels and introducing an energy barrier for the primary electron conduction mechanism by transfer between Mn³⁺ and Mn⁴⁺ ions.¹⁵ In addition, the strained films are also prone to undesirable two-phase behavior.¹⁶,¹⁷ Lattice mismatch strain is progressively relaxed as the films grow thicker.¹⁸ However, in this case, growing thicker films is not an option because thermal strain due to different thermal expansion coefficients for Si and the oxide layers increases as the thickness is increased. Beyond a certain
thickness, which depends on the thermal kinetics of growth, the films are observed to develop microcracks.

We have therefore employed a second lattice matched template layer of Bi$_4$Ti$_3$O$_{12}$ (BTO) between the STO and NSMO layers. Figure 1 shows a typical 2θ-ω scan of a Si/STO/BTO/NSMO multilayer, showing the phase-pure, oriented layers. The BTO out of plane peaks corresponds to a lattice parameter of 32.62 Å, close to the single crystal bulk value of 32.81 Å. The NSMO (002)$_{pseudocubic}$ out of plane peak gives a lattice parameter of 3.85 Å. Note that this is very close to the lattice constant of ~3.86 Å for bulk NSMO, indicating that the lattice mismatch strain has been largely eliminated by the BTO template (table 1). Typical rocking angles for the BTO and NSMO are 0.13° and 0.23° FWHM, respectively, indicating improved NSMO crystallinity due to the BTO buffer. The metal-insulator transition temperature increases to ~200 K and the peak resistivity of the NSMO films is reduced by a factor of ~2, both closer to the optimized unstrained film values. Most importantly for bolometer applications, the maximum TCR is increased to ~13.5 %/K at ~175 K (figure 2), which is more than sufficient for the required sensitivity at LCLS.  

RESULTS AND DISCUSSION

The NSMO films have been photolithographically patterned into 2 × 2 mm$^2$ sensors, cooled inside a vacuum chamber by a low-vibration mechanical pulse-tube refrigerator, stabilized at the temperature of maximum TCR, and exposed to pulsed 532 nm radiation from a commercial Nd-YAG calibration laser (Coherent Minilite-I). Figure 3 shows the sensor response at pulse energy of 1.5 mJ when the 5 ns laser pulse is focused to ~1 mm FWHM and hits the backside of the Si substrate directly opposite the NSMO sensor. Note that in addition to the
expected thermal signal, there are two fast athermal transients in the response whose presence
does not depend on the presence of the NSMO film, or the presence of piezoelectric buffers, or
the application of a bias voltage. The first one (a) is consistent with electron-hole separation
during diffusion due to their different mobilities (Demember effect). The second one (b) is
consistent with the diffusion of thermally generated majority carriers in the Si substrate from higher
to lower temperature regions (transient Seebeck effect). The sensor must be designed such that
both transients have fully decayed before the thermal signal peaks, and can therefore not be
designed for operation much below ~150 K where the thermal signal rise time is much faster
For the prototype NSMO sensor discussed in figure 3, the transients have fully decayed after
~200 µs, so that the peak response at t = 250 µs is linear with incident pulse energy over the
energy range of interest for LCLS (inset figure 3). Once the transients have decayed, both the
peak signal and its integral can be used as measures of the incident energy, with the integral
being somewhat less sensitive to beam jitter and variations X-ray absorption length over the
LCLS energy range from 0.8 to 8 keV. The observed signal decay times of ~10 ms are set by
the diffusivity in Si and by the thermal coupling of the Si chip to the Cu chip holder and are three
orders of magnitude faster than those of conventional cryoradiometers.

CONCLUSION

These results demonstrate the feasibility of building a fast rare-earth manganite sensor
based on a Si/STO/BTO/NSMO multilayer with high sensitivity and good linearity for total
energy measurements at future free-electron X-ray laser facilities. Future work will focus on
further reducing the 1/f noise to increase sensitivity at low FEL energies, and on reducing the
response time for full compatibility with 120 Hz operation at LCLS. The latter will likely
necessitate a suppression of the athermal transients through the appropriate choice of dopants in
the Si substrate, so that faster operation at lower temperatures is possible without interference of the transients with the thermal signal.

ACKNOWLEDGEMENTS

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. We acknowledge support from the undergraduate research grants to Sanjay Adhikari, Rajeh Mundle, David Cox and Anthony Davidson III from the Jess and Mildred Fisher College of Science and Mathematics, Towson University. Thanks are due to Jeff Klupt for help with laboratory instrumentation. RK acknowledges support from the Cottrell College Science Award from the Research Corporation through grant CC 6291.
REFERENCES


Figure 1: Diffraction (2θ/ω) scan of the (00l) peaks of a 800 Å Nd$_{0.67}$Sr$_{0.33}$MnO$_3$ (NSMO) film on Si, using a 100 Å SrTiO$_3$ buffer (STO) grown by MBE and a 340 Å Bi$_4$Ti$_3$O$_{12}$ buffer grown by PLD.
Figure 2: Metal-insulator transition in a 800 Å NSMO film of BTO-STO-buffered Si. The resistance peaks at ~201 K, and the TCR has a maximum value of ~12 %/K at ~176 K.
Figure 3: Laser induced response of a prototype total energy monitor. Note that the thermal signal (solid line) agrees with finite element simulations (dotted line), but is preceded by two non-thermal fast transients due to the Dember effect (a) and due to the transient thermoelectric effect (b). The inset shows the linearity of the thermal signal at $t = 250 \, \mu s$ over the energy range of interest for LCLS.
Table 1: Summary of bulk and film characteristics.

<table>
<thead>
<tr>
<th></th>
<th>Si (cubic)</th>
<th>SrTiO$_3$ (cubic)</th>
<th>Bi$_4$Ti$<em>3$O$</em>{12}$ (tetragonal)</th>
<th>Nd$<em>{2/3}$Sr$</em>{1/3}$MnO$_3$ (pseudocubic)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Bulk thermal expansion coefficient $\alpha$</strong></td>
<td>$2.49 \times 10^{-6}$ K$^{-1}$ at 300K</td>
<td>$3.23 \times 10^{-5}$ K$^{-1}$ 300 to 2000K</td>
<td>~$3 \times 10^{-3}$ K$^{-1}$</td>
<td></td>
</tr>
<tr>
<td><strong>Bulk lattice parameters at 300K</strong></td>
<td>$a = 5.4309\text{Å}$</td>
<td>$a = 3.905\text{Å}$</td>
<td>$a = 3.861\text{Å}$</td>
<td>$a = 3.87\text{Å}$</td>
</tr>
<tr>
<td></td>
<td>$a/\sqrt{2} = 3.840\text{Å}$</td>
<td></td>
<td>$c = 32.81\text{Å}$</td>
<td></td>
</tr>
<tr>
<td><strong>Si/STO/NSMO film:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lattice parameters</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rocking angles</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$a_{\perp} = 3.891\text{Å}$</td>
<td></td>
<td>$a_{\perp} = 3.82\text{Å}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>FWHM = 0.16$^\circ$</td>
<td></td>
<td>FWHM = 0.48$^\circ$</td>
<td></td>
</tr>
<tr>
<td><strong>Si/STO/BTO/NSMO film:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lattice parameters</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rocking angles</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$c = 32.62\text{Å}$</td>
<td></td>
<td>$a_{\perp} = 3.85\text{Å}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>FWHM = 0.13$^\circ$</td>
<td></td>
<td>FWHM = 0.23$^\circ$</td>
<td></td>
</tr>
</tbody>
</table>