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Total Energy CMR Production

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Total Energy CMR Production

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Summary:

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

Change History Log

Rev Number	Revision Date	Sections Affected	Description of Change
000	2008/8/1	All	Initial Version

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Auspices Statements

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Executive Summary:

The following outlines the optimized pulsed laser deposition (PLD) procedure used to prepare $Nd_{0.67}Sr_{0.33}MnO_3$ (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:

Abbreviation	Material	Approximate Thickness
YSZ	$Y:ZrO_2$ (8 mole % Y_2O_3 in ZrO_2)	Initial Bottom Layer: 10 nm Second over-Layer: 240 nm
CeO	CeO_2	22.5 nm
BTO	$Bi_4Ti_3O_{12}$	17 nm
NSMO	$Nd_{0.67}Sr_{0.33}MnO_3$	160 nm

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_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)
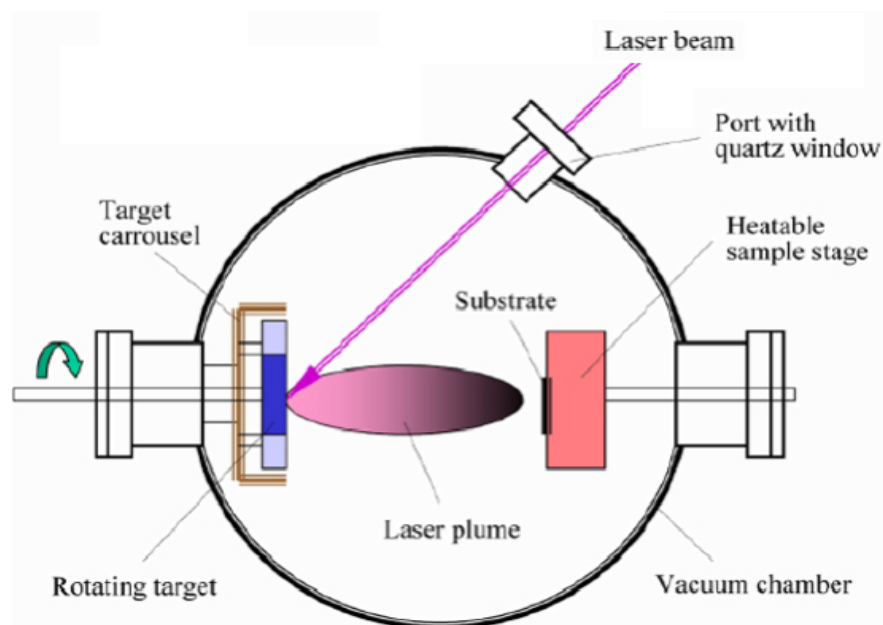
Pulsed Laser Deposition

Fig.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 ~ 180 K.

Table 2: PLD Parameters for the multilayer scheme

Material	Growth temperature (°C)	Pre-ablation conditions	Laser Pulse Energy & Pulse Repetition Rate	Ambient gas pressure during growth and/or cool down	Heating and cooling rates
YSZ (Initial layer, ~10 nm)	780	Vaccum; 1500 pulses of 580 mJ at 10 Hz	580 mJ 10 Hz (500 pulses)	10^{-5} Torr (air)	Heated to 750 °C at 20 °C /min
YSZ (Second layer, ~240 nm)	780	-	580 mJ, 10 Hz (18000 pulses)	4×10^{-4} Torr oxygen (O_2)	Cooled to 750 °C at 3 °C / min
CeO (~22.5 nm)	750	580 mJ 10 Hz (1500 pulses)	580 mJ 10 Hz (750 pulses)	400 mTorr oxygen (O_2)	Cooled to 650 °C at 3 °C / min
BTO (~17 nm)	650	580 mJ 10 Hz (1500 pulses)	580 mJ 10 Hz (750 pulses)	400 mTorr O_2	Heated to 790 °C at 5 °C /min
NSMO (~160 nm)	790	580 mJ 10 Hz (1500 pulses)	580 mJ, 10 Hz (8000 pulses)	400 mTorr O_2 (growth) 530 Torr O_2 (cooling)	Cooled to room temperature at 1 °C /min

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 less than ~ 5×10^{-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/cm^2 [This initial layer of YSZ serves to de-oxygenate the native SiO_2 layer on the substrate].

9. The turbo pump is switched to speed control mode, the oxygen inlet valves are opened and a pressure of 1×10^{-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 O_2 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 CeO_2 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 $TCR \equiv 1/R \times \partial R/\partial T$, are shown in figure 2. Figure 3 shows a typical X-ray 2Θ-Θ scan of a high-quality sample. X-ray φ-scans indicating epitaxial alignment of the different layers are shown in figure 4.

Sample Name	Resistance	X-ray Diffraction
NSMOA119 $BTO/CeO_2/YSZ/$floatzone pSi	2 probe: $3.3 - 5$ kΩ 4 probe: $T_{peak} = 218$ K $TCR_{max} = 13\%$ $R_{peak} = 2950$ Ω	High intensity peaks $NSMO(002)$ $FWHM_{rock} =$ 0.55°
NSMOA122 $BTO/CeO_2/YSZ/$floatzone pSi	2 probe: $3 - 3.8$ kΩ	High intensity peaks $NSMO(002)$ $FWHM_{rock} =$ 0.75°
NSMOA124 $BTO/CeO_2/YSZ/$floatzone pSi	2 probe: $2.7 - 3.7$ kΩ	High intensity peaks $NSMO(002)$ $FWHM_{rock} =$ 0.59°
NSMOA125 $BTO/CeO_2/YSZ/$floatzone pSi	2 probe: $3 - 3.9$ kΩ	High intensity peaks $NSMO(002)$ $FWHM_{rock} =$ 0.61°
NSMOA126 $BTO/CeO_2/YSZ/$low ρ nSi	2 probe: 3.5 kΩ	High intensity peaks $NSMO(002)$ $FWHM_{rock} =$ 0.61°
NSMOA128 $BTO/CeO_2/YSZ/$low ρ nSi	2 probe: 5 kΩ	High intensity peaks $NSMO(002)$ $FWHM_{rock} =$ 0.79°
NSMOA130 $BTO/CeO_2/YSZ/$low ρ nSi	2 probe: 5 kΩ	High intensity peaks $NSMO(002)$ $FWHM_{rock} =$ 0.57°
NSMOA133 $BTO/CeO_2/YSZ/$low ρ nSi	2 probe: 5 kΩ	High intensity peaks $NSMO(002)$ $FWHM_{rock} =$ 0.84°

In addition, the following samples, sent in a prior shipment, are comparable in properties to the final set of 8 samples above:

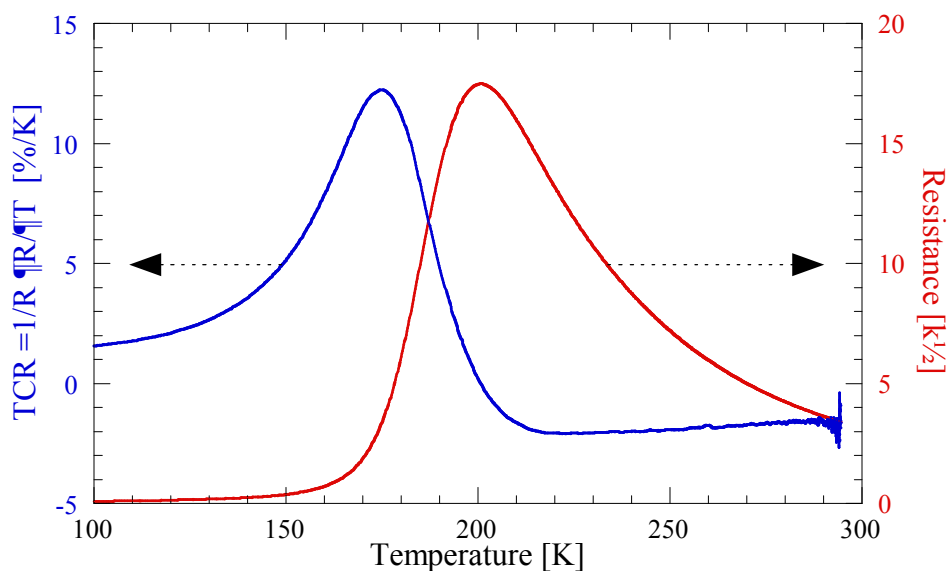| Sample Name	Resistance	X-ray Diffraction
NSMOA112 BTO/CeO$_2$/YSZ/floatzone pSi	2 probe: 3.3 – 4 kΩ 4 probe: T_{peak} = 178 K TCR_{max} = 6% R_{peak} = 5400 Ω Same as final recipe *except may have started NSMOA deposition at 780°C instead of waiting until 790°C.*	High intensity peaks NSMO(002) FWHM$_{rock}$ = 0.52°
NSMOA113 BTO/CeO$_2$/YSZ/floatzone pSi	2 probe: 5 – 7 kΩ 4 probe: T_{peak} = 205 K TCR_{max} = 11.5% R_{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$_{rock}$ = 0.51°
NSMOA115 BTO/CeO$_2$/YSZ/floatzone pSi	2 probe: 4 – 5 kΩ 4 probe: T_{peak} = 217 K TCR_{max} = 12.7% R_{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$_{rock}$ = 0.52°

Fig. 2: Resistance vs temperature for an optimized NSMO film
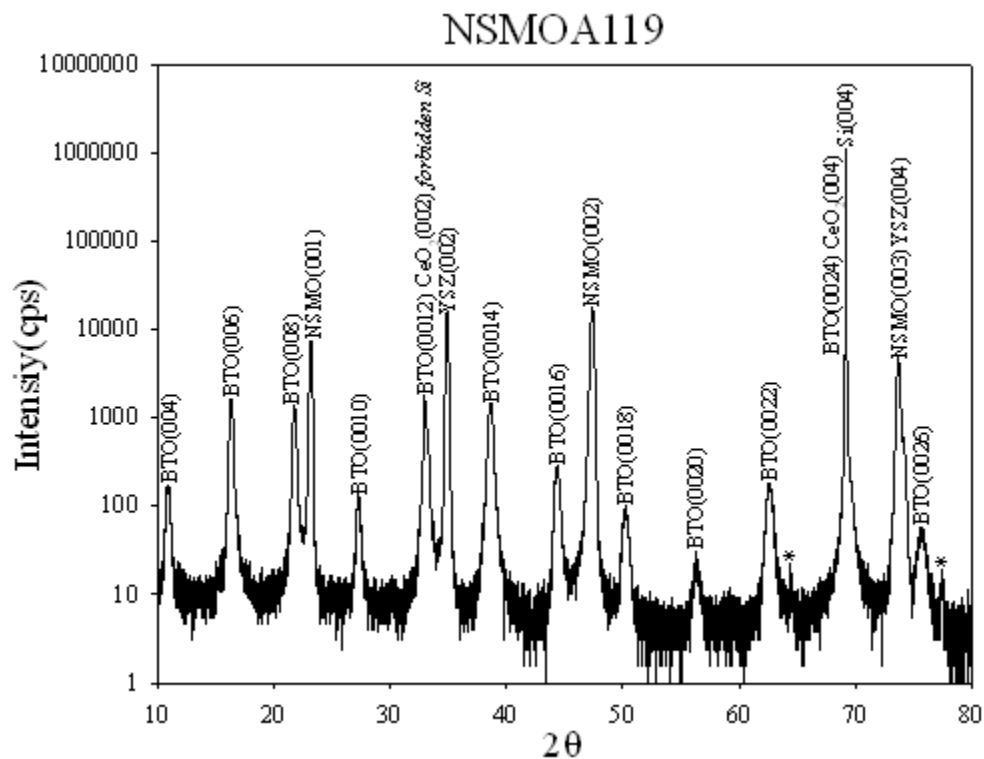

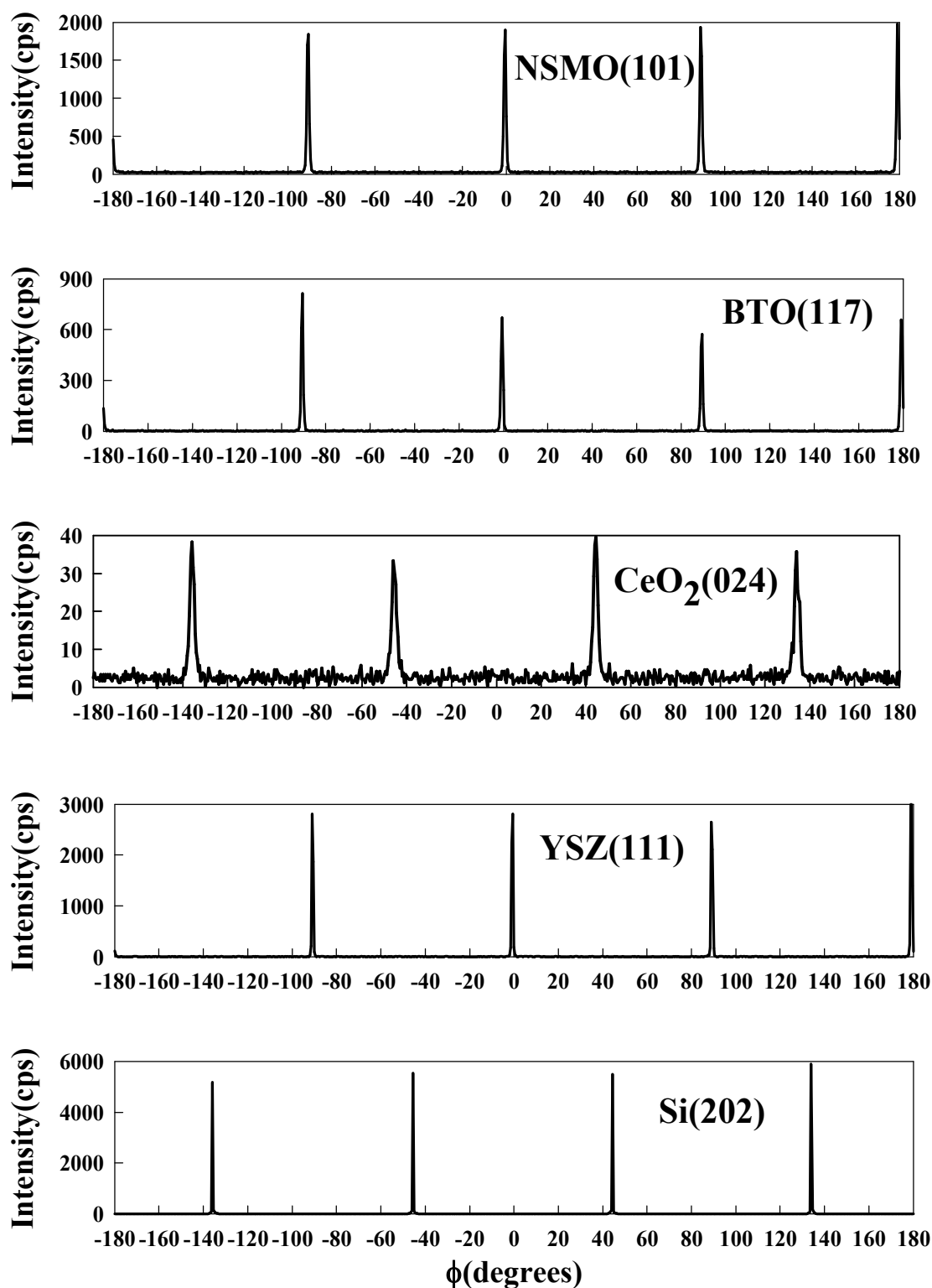Fig. 3: 2Θ-Θ X-ray diffraction scan of an optimized NSMO film.

Fig. 4: X-ray diffraction φ-scan, showing epitaxial alignment of the different layers in the multilayer structure NSMO[110] // BTO[100] // CeO2[100] // YSZ[100] // Si[100].