DE-FG02-06ER46273

Final Report

"Oxide Interfaces: emergent structure and dynamics"

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Project Period 6/1/2012 to 5/31/2016

SUMMARY

This Final Report describes the scientific accomplishments that have been achieved with support from grant DE-FG02-06ER46273 during the period 6/1/2012– 5/31/2016. The overall goals of this program were focused on the behavior of epitaxial oxide heterostructures at atomic length scales (Ångstroms), and correspondingly short time-scales (fs -ns). The results contributed fundamentally to one of the currently most active frontiers in condensed matter physics research, namely to better understand the intricate relationship between charge, lattice, orbital and spin degrees of freedom that are exhibited by complex oxide heterostructures. The findings also contributed towards an important technological goal which was to achieve a better basic understanding of structural and electronic correlations so that the unusual properties of complex oxides can be exploited for energy-critical applications. Specific research directions included: probing the microscopic behavior of epitaxial interfaces and buried layers; novel materials structures that emerge from ionic and electronic reconfiguration at epitaxial interfaces; ultrahigh-resolution mapping of the atomic structure of heterointerfaces using synchrotron-based x-ray surface scattering, including direct methods of phase retrieval; using ultrafast lasers to study the effects of transient strain on coherent manipulation of multi-ferroic order parameters; and investigating structural ordering and relaxation processes in real-time.

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1. Research Progress and Accomplishments

Over the period of this grant, which was initiated in 2006, several important milestones have been achieved as summarized in the list below. A more detailed description of the results from the most recent funding period (2012 -2016) follows.

- First application of the COBRA (Coherent Bragg Rod Analysis) phase-retrieval method for direct determination of interfacial atom arrangements in complex oxide heterostructures.
- First application of COBRA in resonant scattering mode enabling the clean separation of the effects of chemical composition and strain at interfaces.
- Determined the structural basis of the conducting interface in $LaAlO_3$ –$SrTiO_3$.
- Quantitative explanation of domain structures in ultrathin ferroelectric films.
- First structural study of onset of magneto-resistance in ultrathin $La_{1-x}Sr_xMnO_3$ films.
- First demonstration of asynchronous optical sampling fiber laser for wide-band pump-probe.
- Identification of a new phase of BiFeO3 with a tetragonal structure that is "untilted" by substrate interactions.
- Observation of a unique doping mechanism which leads to polarization enhancement in the ferroelectric $BaTiO_3$ epitaxially grown on $SrTiO_3$ with a $LaTiO_3$-$LaAlO_3$.

During the most recent funding period (2012- 2016) this grant has supported research leading to 8 refereed journal publications, 2 invited conference presentations, and the Ph.D. dissertations of 2 graduate students. A summary of our most important research findings from the project period 2012 -2016 follows.

In the current project period we focused on several experiments which probe the interface structure of complex oxides grown on various perovsike substrates with the aim of better understanding the role of epitaxial thin-film strain on the interesting properties of these materials. In particular, we are interested in probing the atomic details of the structure at the heterointerface motivated by the fact that novel correlated electron phenomena are known to occur at such interfaces. Here we summarize our progress on these experiments, mostly carried out at the Advanced Photon Source. Highlights include the report of a new tetragonal phase which appears in ultrathin films (less than 20 unit cells thick) and is clearly driven by the boundary conditions at the interface between the substrate and the $BiFeO_3$ film. The work is recently published in the journal Applied Physics Letters: Materials. Two follow-on papers were published on related phenomena in $BiFeO_3$, the latter in collaboration with Hans Christen's group at ORNL.

1.1. Untilting $BiFeO_3$: the influence of substrate boundary conditions in ultra-thin $BiFeO_3$ on $SrTiO_3$.

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As one of the few room temperature multiferroic materials (ferroelectric: $T_C \sim 1103$ K, antiferromagnetic: $T_N \sim 643$ K), bismuth ferrite ($BiFeO_3$) has been studied extensively in recent years. The bulk form of $BiFeO_3$ is known to have a rhombohedrally distorted quasi-cubic perovskite structure with an $a^-a^-a^-$ octahedral tilt pattern, exhibiting both anti-ferrodistortive displacements and a spontaneous polarization along the ⟨111⟩ pseudocubic axes. When epitaxial $BiFeO_3$ thin films are grown under compressive strain on (001)-oriented perovskite substrates, several studies have reported that the polarization direction is tilted towards the [001] out-of-plane direction, while maintaining a significant in-plane component, depending on the amount of epitaxial strain from the substrate. This effect is accompanied by a significant enhancement of the spontaneous polarization and a series of phase transitions from rhombohedral (R), for small strains, to R-like monoclinic (M_A) to T-like monoclinic (M_C) and to tetragonal (T) for larger strains, the latter two of which exhibit a giant c/a ratio. Bismuth ferrite films (thickness >26 nm) grown on (001) $SrTiO_3$ (STO) substrates (−1.4% compressive strain) exhibit the R-like monoclinic structure (M_A) with a c/a ratio close to unity.

Previous studies have shown that the effects of the perovskite heterointerfaces generally extend over only a few unit cells. In particular, ultra-thin $BiFeO_3$ films grown on (001) $SrTiO_3$ substrates with a $SrRuO_3$ buffer layer showed evidence for a transition to tetragonal symmetry. Also, it has been reported that $BiFeO_3$ films grown on (001) $SrTiO_3$ can have a tetragonal structure with a giant c/a ratio, resulting from the higher strain induced by a Bi_2O_3 layer, which can be formed between the film and the substrate.

In this project, we studied the thickness dependence of the $BiFeO_3$ thin film structure in the ultra-thin regime under moderate compressive strain from (001) $SrTiO_3$ substrates. We found that the transition from monoclinic to tetragonal is accompanied by a change in the octahedral tilt pattern which reflects the increase in symmetry, and in fact definitively establishes the ultrathin-film structure as tetragonal. This is important for several reasons: first, device applications normally require a single-domain state, which the lower-symmetry bulk-like mononclinic phases do not generally support; and secondly, the new tetragonal phase favors a polar alignment *normal* to the plane of the film, a geometry that is favorable for planar devices with electrodes above and below the ferroic film. A correct determination and deeper understanding of the ultra-thin regime of the $BiFeO_3$ film structure is therefore critical in the sense that the multiferroic and electronic properties depend strongly on the film heteroepitaxy. This is essential for applications of multiferroics such as low-power electronics and energy storage.

The $BiFeO_3$ thin films in this project were grown in Darrell Schlom's lab at Cornell by reactive molecular-beam epitaxy (MBE) on $SrTiO_3$ (001) substrates. Synchrotron x-ray diffraction experiments were carried out at beamlines 13-BM-C, 33-ID-D, and 33-BM-C of the Advanced Photon Source. To identify the symmetry of the $BiFeO_3$ films, high-resolution three-dimensional reciprocal space maps (3D RSMs) were measured around high-order film Bragg peaks and half-integer order peaks, which are sensitive to the anti-ferrodistortive octahedral tilting pattern. Using a PILATUS 100K area detector, the intensity distribution around each peak was measured in a series of single scans along the L-direction as a set of two-dimensional reciprocal space slices. These were then used to reconstruct the 3D RSMs.

Examples of the RSMs obtained are shown in Fig. 1(a–c) as (HH)L slices through the 3D-RSMs around the 335 peaks for three different film thicknesses. We observed that the signal from the 50 unit cell (UC) thick film [Fig. 1(a)] is split into three distinct peaks. This splitting pattern corresponds to the well-known M_A monoclinic structure in the presence of four domains that tilt in different directions, reported for $BiFeO_3$ films on $SrTiO_3$ with thickness > 26 nm. For the 20 UC film [Fig. 1(b)], however, the splitting is less pronounced, while for 10 UC [Fig. 1(c)], only a single peak is observed (although it is broadened in the out-of-plane direction due to the finite thickness of the film). These findings prove that there is a structural phase transition as the film thickness decreases. Additional scans, in particular through half-order reciprocal space positions which probe the octahedral tilting in the film, provide definitive proof of the tetragonal symmetry and show that the interface structure is key to the occurrence of this transition.

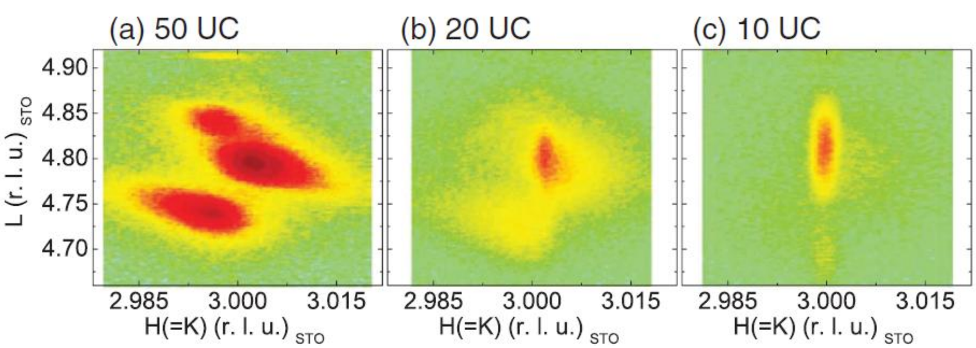

Fig. 1: a –c. (HH)L map of the 335_{pc} peak for 50 UC, 20 UC and 10 UC of $BiFeO_3$ films grown epitaxially on $SrTiO_3$ (001) substrates. Here $_{pc}$ refers to pseudo-cubic symmetry and all reciprocal lattice positions are given in terms of the $SrTiO_3$ substrate reciprocal unit cell. Note that the weak feature at L~4.7 r.l.u. is a finite thickness fringe rather than a Bragg peak.

Ongoing work related to this project includes a detailed analysis of the Bragg rod scattering (Fig. 2) of the ultrathin (tetragonal) BiFeO3 films with the goal of determining the atomic positions with high resolution on a layer-by-layer basis. We used the COBRA direct phase retrieval technique for this task, developed by the PI's group. The complexity of the structure, especially the degrees of freedom associated with the octahedral tilting, necessitate direct methods of phase determination.

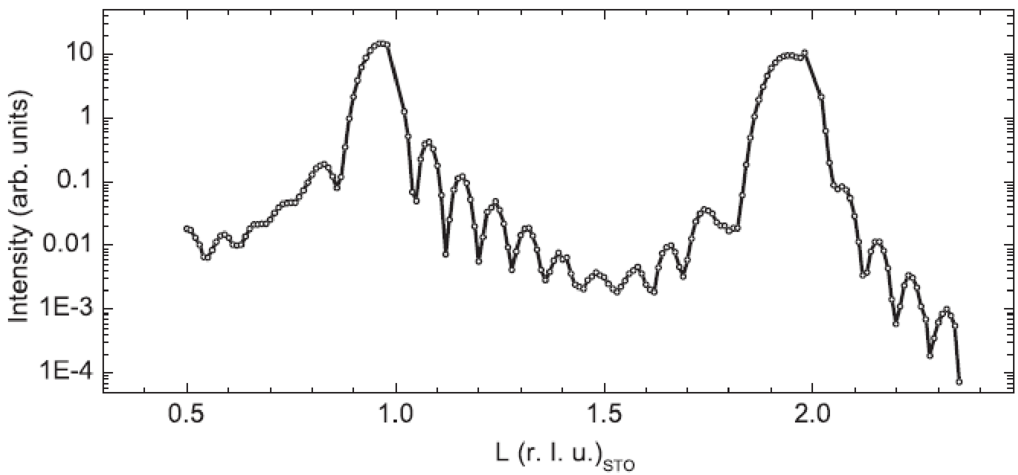

Fig. 2: 00L Bragg-rod scan of tetragonal 10 unit cell ultrathin $BiFeO_3$ film grown on $SrTiO_3$ (001). The solid line is a guide to the eye.

1.2 Origin of thickness dependence of structural phase transition temperatures in highly strained $BiFeO_3$ thin films

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In Section 1.1 we described how epitaxial growth of $BiFeO_3$ on an untilted substrate ($SrTiO_3$) can lead to a novel tetragonal structure which is "untilted" around the [110] axis in the interface region close to the substrate. In this example, we use a different substrate, $LaAlO_3$, which has a significantly larger mismatch with $BiFeO_3$ than $SrTiO_3$ and leads to a different set of structural transitions. Interestingly, the $BiFeO_3$ is again

strongly influenced by the substrate and also takes on the in-plane tilt pattern of the substrate. Two structural phase transitions were investigated in the highly strained $BiFeO_3$ thin films as a function of film thickness and temperature via synchrotron x-ray diffraction.
Both transition temperatures (upon heating: monoclinic MC to monoclinic MA to tetragonal) decrease as the film becomes thinner. A film-substrate interface layer, evidenced by half-order peaks, contributes to this behavior, but at larger thicknesses (above a few nanometers), the temperature dependence results from electrostatic considerations akin to size effects in ferroelectric phase transitions, but observed here for structural phase transitions within the ferroelectric phase. For ultra-thin films, the tetragonal structure is stable to low temperatures.

$BiFeO_3$ films grown epitaxially on $SrTiO_3$ substrates as described above are subject to a moderate -1.4% compressive strain which we found stabilizes a novel tetragonal phase when the film thickness is less than 20 unit cells thick. We wished to investigate what the effect of epitaxial strain was on this transition. Therefore, we studied the structural behavior of $BiFeO_3$ films grown on a substrate, $LaAlO_3$, that has a significantly larger mismatch, leading to a -4.3% compressive strain. $LaAlO_3$ is also of interest as one component of the $LaAlO_3$-$SrTiO_3$ interface that exhibits an unusual quasi two-dimensional electron gas behavior, which the PI's group has studied in previous stages of this program.

These studies of $BiFeO_3$ (BFO) films grown on $LaAlO_3$ (LAO) were carried out in collaboration with the group of Hans Christen at Oak Ridge National Laboratory. The samples were grown epitaxially by pulsed laser deposition in the Christen lab and x-ray scattering studies were performed at the Advanced Photon Source. Since 5nm BFO films on LAO substrates are known to exhibit M_A monclinic structure at room temperature, we prepared two thinner films (4 nm and 2.4nm) to check for the presence of additional transitions in the ultrathin regime. In particular we were interested to know if the ultrathin samples would transform to a tetragonal phase when the film thickness is reduced. We were also interested in whether a transition might occur when the temperature was lowered below room temperature. Therefore we studied the structure of these ultrathin samples using a closed-cycle He cryostat to cool the sample temperature to 30K.

Figure 3 shows (HH)L reciprocal mapping for H =1,2,3 for both 4nm and 2.4 nm BFO films on the high compressive strain (LAO) substrate. For the 4nm film, a peak splitting is observed mainly in the L direction with increasing separation between the split peaks with increasing $q_{//}$. This, and other similar scans, indicates that the 4 nm film still exhibits M_A monoclinic symmetry. For the 2.4 nm film on the other hand, a totally different behavior is observed. Apart from the peaks being elongated along L, which is expected for thinner films, there is no clear 2-fold or 3-fold splitting and the peak is not dependent on $q_{//}$. This shows that the highly strained films grown on LAO also show the disappearance of the peak splitting in the ultrathin regime. More detailed scans on a larger set of Bragg-peaks proved that the observed phase is also tetragonal, analogous to the structure seen in the less strained BFO film grown on $SrTiO_3$ described above. The larger compressive stress apparently drives the transition thickness to smaller dimensions, indicating again that the substrate interface plays a crucial role in the formation of the tetragonal phase.

Temperature dependence -In addition to these studies as a function of film thickness, we have studied the peak splitting pattern in films of 5nm and 4 nm thickness while cooling the samples to 30K. When the samples are cooled we see a transition from 3-fold splitting (indicating M_A symmetry) to 2-fold splitting, indicating M_C symmetry. We are now extending these studies to even lower temperatures to examine whether these highly strained films (thickness > 4nm) will eventually transform to the tetragonal phase as a function of temperature. In this way we can separate the effects of temperature from pure strain effects.

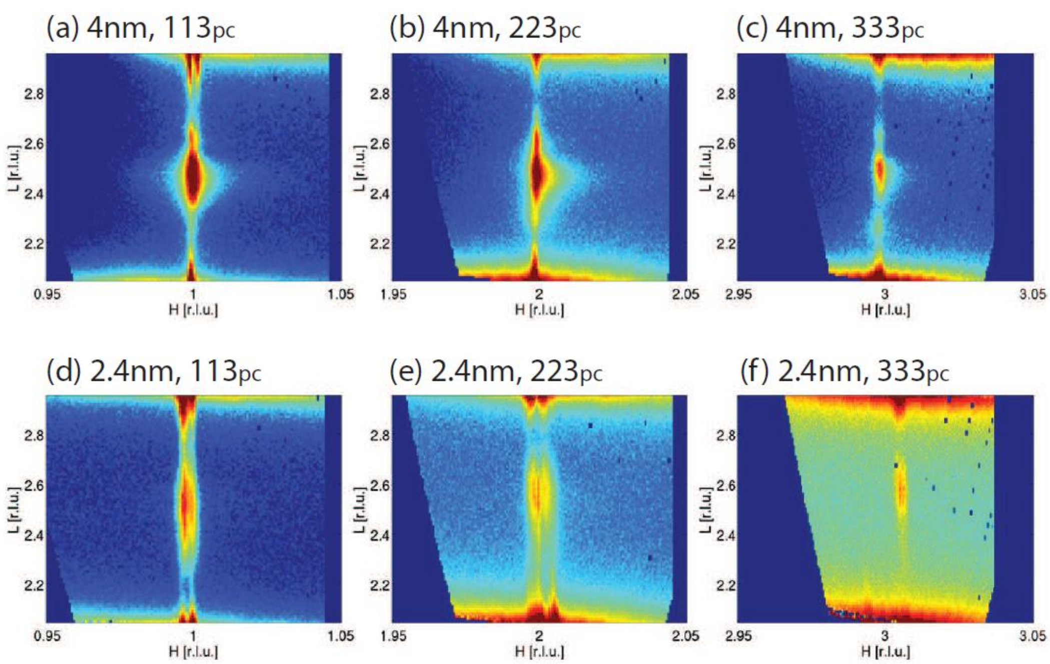

Fig. 3a-c: HHL map of the $HH3_{pc}$ peak (H=1,2,3) for 4nm $BiFeO_3$ film on LAO substrate; d-f: $HH3_{pc}$ peaks for 2.4 nm BFO film. Note that the split features along H direction (e.g., in d and e) are due to mosaic structure in the LAO substrate and are not indicative of symmetry changes in the film.

This work on highly strained BFO is the topic of the PI's graduate student's doctoral dissertation (Yongsoo Yang).

A third example of the work performed in this project consists of a collaborative study between the PI's group and a theory group (Valentino Cooper) at ORNL. The aim was to gain a deeper understanding of the experimental results that were obtained on strain-induced structural phase transformations in multiferroic $BiFeO_3$ films.

1.3 Understanding Strain-Induced Phase Transformations in $BiFeO_3$ Thin Films

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Experiments demonstrated that under large epitaxial strain a coexisting striped phase emerges in $BiFeO_3$ thin films, which comprises a tetragonal-like (*T ′*) and an intermediate *S ′* polymorph. It exhibits a relatively large piezoelectric response when switching between the coexisting phase and a uniform *T ′*phase. This strain-induced phase transformation is investigated through a synergistic combination of first-principles theory and experiments. The results show that the *S ′* phase is energetically very close to the *T ′* phase, but is structurally similar to the bulk rhombohedral (*R*) phase. By fully characterizing the intermediate *S ′* polymorph, it is demonstrated that the flat energy landscape resulting in the absence of an energy barrier between the *T ′* and *S ′* phases fosters the above-mentioned reversible phase transformation. This ability to readily transform between the *S ′* and *T ′* polymorphs, which have very different octahedral rotation patterns and *c* / *a* ratios, is crucial to the enhanced piezoelectricity in strained $BiFeO_3$ films. Additionally, a blueshift in the band gap when moving from *R* to *S ′* to *T ′* is observed. These results emphasize the importance of strain engineering for tuning electromechanical responses or, creating unique energy harvesting photonic structures, in oxide thin film architectures.

2. List of Publications from work supported by Grant DE-FG02-06ER46273

[Acknowledgments section reproduced for each paper; personnel supported are underlined]

1. Y. Yang, C.M. Schlepuetz, C. Adamo, D.G. Schlom, and R. Clarke, “Untilting $BiFeO_3$: the influence of substrate boundary conditions in ultrathin $BiFeO_3$ on $SrTiO_3$”, *Applied Physics Letters: Materials* 1, 052102 (2013).

The authors wish to thank J. W. Freeland and V. Stoica for helpful discussions. This work was supported by the U.S. Department of Energy (Contract No. DE-FG02-06ER46273). The film synthesis work (at Cornell University) was supported by the Army Research Office through Agreement No. W911NF-08-2-0032. The X-ray diffraction experiments were performed at sectors 13-BMC (GeoSoilEnviroCARS), 33-IDD (XSD), and 33-BMC (XSD) at the APS. Excellent beamline support by P. J. Eng, J. Stubbs, Z. Zhang, E. Karapetrova, and the staff of the APS is gratefully acknowledged. GeoSoilEnviroCARS is supported by the National Science Foundation - Earth Sciences (EAR-0622171) and Department of Energy - Geosciences (DE-FG02-94ER14466). The use of the APS was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

2. D.P. Kumah, Y.Yacoby, S.A. Pauli, P.R. Willmott, R.Clarke, “La-doped $BaTiO_3$ heterostructures: compensating the polarization discontinuity”, *APL Materials* 1, 062107 (2013).

This work was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences (Contract No. DE-FG02-06ER46273, PI: RC). Y.Y. acknowledges support from the Israel Science Foundation Grant No. 1005/11.

3. Yongsoo Yang, Christianne Beekman, Wolter Siemons, Christian M. Schleputz, Nancy Senabulya, Roy Clarke and Hans Christen, Origin of thickness dependence of structural phase transition temperatures in highly strained $BiFeO_3$, thin films, *APL Materials* 4, 036106 (2016)

Research at ORNL was supported by the U. S. Department of Energy (DOE), Basic Energy Sciences (BES), Materials Science and Engineering Division (H.M.C., W.S., and C.B.). Research at Michigan was supported by DOE Contract No. DE-FG02-06ER46273 (PI: R.C.). Synchrotron x-ray experiments were performed at Sectors 33-BM-C and 33-ID-D at the APS. Excellent beamline support by Z. Zhang, E. Karapetrova, and the staff of the APS is gratefully acknowledged. The use of the APS was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

4. Hemant Dixit, Christianne Beekman, Christian M. Schlepütz, Wolter Siemons, Yongsoo Yang, Nancy Senabulya, Roy Clarke, Miaofang Chi, Hans M. Christen, and Valentino R. Cooper, Understanding Strain-Induced Phase Transformations in $BiFeO_3$ Thin Films, *Advanced. Science* ***2***, 150004 (2015).

This research was supported by the US Department of Energy (DOE), Office of Science, Basic Energy Sciences (BES), Materials Sciences and Engineering Division (authors H.D. V.R.C.: fi rst-principles modeling; C.B.,W.S., and H.M.C.: film growth, XRD, AFM, PFM), the Offi ce of Science Early Career Research Program (V.R.C) and the Scientific User Facilities Division (author M.C.: STEM). User projects were supported at ORNL's Center for Nanophase Materials Sciences and ANL's Advanced Photon Source, which are DOE Offi ce of Science user facilities. This research used resources of the National Energy Research Scientific Computing Center, which is supported by the DOE Office of Science under Contract No. DE-AC02-05CH11231. Work in Michigan was supported by US Department of Energy (Contract No. DE-FG02-06ER46273, PI: R.C.).

5. Y. Yang, C.M. Schlepütz, F. Bellucci, M.W. Allen, S.M Durbin, R. Clarke, Structural investigation of ZnO O-polar $(000\bar{1})$ surfaces and Schottky interfaces, *Surface Science*, **610**, 22-26 (2013).

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2.1 Other papers acknowledging this grant:

6. Shaurjo Biwas, Yongsoo Yang, Christian M. Schlepütz, Nadav Geva, Randall L. Headrick, Ron Pindak, Roy Clarke, and Max Shtein, "Spatial mapping of morphology and electronic properties of air-printed pentacene thin films" Advanced *Functional Materials* **24**, 3907-3916 (2014).

The authors MS and SB thank the Air Force Office of Scientific Research (AFOSR) for its Presidential Early Career Award for Scientists and Engineers (PECASE), Award No. FA9550-09-1-0109, for supporting the development of the GF-OVJP technique, analysis of compressible hydrodynamics, and its application to deposition of organic TFT materials and devices performed in this work. MS, RC, SB,YY and CMS acknowledge funding from the Center for Solar and Thermal Energy Conversion, an Energy

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7. I. Cour, P.V. Chinta, C.M. Schlepuetz, Y. Yang, R. Clarke, R. Pindak, R.L. Headrick, "Origin of stress and enhanced carrier transport in solution-cast organic semiconducting films", *J. Appl. Phys*. 114, 093501 (2013).

The authors thank: Steve Lamarra and Christie Nelson for their assistance with the beamline instrumentation and setup for the synchrotron x-ray experiments at the NSLS; Arthur Woll and Thomas Howard for assistance during the x-ray diffraction measurements conducted at the Cornell High Energy Synchrotron Source (CHESS); Michael Ghebreab for assisting with PTS treatment on Si/SiO_2 wafers. IC, PVC, and RLH were supported by Grant No. DE-FG02-07ER46380 from the U.S. Department of Energy (DOE), Office of Basic Energy Sciences, Division of Materials Sciences and Engineering. The pen writer instrumentation development was supported by the National Science Foundation Major Research Instrumentation program under Grant No. DMR-0722451. CMS, YY, and RC were supported in part by Grant No. DE-FG02-06ER46273 from the U.S. DOE, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering. Use of the NSLS was supported by the U.S. DOE, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-98CH10886. Use of the CHESS was supported by the NSF and the National Institutes of Health/National Institute of General Medical Sciences under NSF award DMR-0936384.

8. O. Shalev, S. Biswas, Y.Yang, T. Eddir, W. Lu, R. Clarke, M. Shtein, Growth and modelling of spherical crystalline morphologies of molecular materials, *Nature Communications* **5**, 5204 (2014).

This work was supported in part by the US Department of Energy (DOE), Office of Basic Energy Sciences, as part of the Center for Solar and Thermal Energy Conversion, an Energy Frontier Research Center (Award No. DE-SC0000957) and also by DOE under Contract No. DE-FG02–06ER46273 (PI: RC). NSF and AFOSR supported the construction of the deposition apparatus. We would also like to acknowledge Matthew Sykes for fruitful discussions while writing the manuscript, Anton Li for help in writing the model, Onye Anatohu for initial experiments with GF-OVJP system, Christian Schlepütz and Nancy Senabulya for their help in the X-ray experiments and Bradley Frieberg for help with spectroscopic ellipsometry. The XRD measurements were performed at beamline X21 at the NSLS and at Sectors 13-BM-C (GeoSoilEnviroCaRS), and 33-ID-D (XSD) at the APS. We thank R. Pindak, C. Nelson, S. LaMarra, C. M. Schlepütz, Z. Zhang, E. Karapetrova, Ishviene Cour, Randall Headrick and the staff of the APS and NSLS for their excellent beamline support. The use of NSLS was supported by the DOE, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-98CH10886. GeoSoilEnviroCARS is supported by the National Science Foundation—Earth Sciences (EAR-1128799) and Department of Energy—Geosciences (DE-FG02-94ER14466). The use of the APS was supported by the DOE, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

3. Invited Conference Presentations

AMN6: International Conference on Nanoscience and Technology, Auckland, New Zealand, February, 2013; “Ultrafast Ultrasmall – making nanostructures with femtosecond lasers” (plenary invited).

International Conference on Nanoscience and Nanotechnology, Konya, Turkey, August 2016; “New tools for nanofabrication and characterization”.

Earlier papers acknowledging Grant DE-FG02–06ER46273

1. Structural Basis for the conducting interface , between $LaAlO_3$ and $SrTiO_3$, P.R. Willmott, S.A. Pauli, R. Herger, C.M. Schlepűtz, D. Martioccia, B.D.Patterson, B. Delley, R. Clarke, D. Kumah, C. Cionca, and Y. Yacoby, Phys. Rev. Lett. **99**, 155502 (2007).

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2. Real time structural modification of epitaxial FePt thin films under x-ray rapid thermal annealing using undulator radiation, J. R. Skuza, R. A. Lukaszew, E. M. Dufresne, D. A. Walko, C. Clavero, A. Cebollada, C. Cionca, R. Clarke, Appl. Phys. Lett. **90**, 251901 (2007).

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3. Optimizing the planar structure of (111) Au/Co/Au trilayers, D P Kumah, A Cebollada, C Clavero, J M García-Martín, J R Skuza, R A. Lukaszew and R Clarke, J. Phys. D: Appl. Phys. **40**, 2699- 2704 (2007) .

"This work was supported in part by the US Department of Energy, Basic Energy Sciences, under grant DEFG02-06ER46273, the Spanish Ministerio de Educaci´on y Ciencia (PR2005-0017 and MAT2005-05524-C02-01), the Comunidad de Madrid (S-0505/MAT/0194 Nanomagnet) and the CSIC (200650I130). CC acknowledges the Ministerio de Educacion y Ciencia and the FPI Program for financial support."
[DE-FG02-06ER46273 provided support for graduate student D. Kumah, and x-ray analysis of samples; partial travel support for collaborator, A. Cebollada (from IMM, Spain), was also provided from the grant.]

4. Surface magnetoplasmon nonreciprocity effects in noble-metal/ferromagnetic heterostructures , J. B. González-Díaz, A. García-Martín, G. Armelles, J. M. García-Martín, C. Clavero, A. Cebollada, R. A. Lukaszew, J. R. Skuza, D. P. Kumah, and R. Clarke, Phys. Rev. B **76**, 153402 (2007).

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[DE-FG02-06ER46273 supported the work of A. Cebollada during his sabbatical at University of Michigan as a visiting professor. Some of these expenses were shared with the Visiting Scientist Program of the NSF supported FOCUS Center. Note that leveraging is required to receive funds from the FOCUS visitor program.]

5. Spatial coherence properties of a compact and ultrafast laser-produced plasma keV x-ray source, D. Boschetto, G. Mourou, A. Rousse , A. Mordovanakis, Bixue Hou, J. Nees, D. Kumah and R. Clarke, , Appl. Phys. Lett. **90**, 011106 (2007).

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[The work was mainly supported by NSF and is only peripherally related to the current grant (through the use of time-dependent x-ray sources)]

6. Interfacial structure, bonding and composition of InAs and GaSb thin films determined using coherent Bragg rod analysis, C. N. Cionca, D. A. Walko, Y. Yacoby, C. Dorin, J. Mirecki Millunchick, and R. Clarke**,** Phys. Rev. B75, 115306 (2007).

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[Primary support for this work came from NSF DMR-0606048;   DE-FG02-06ER46273 provided some travel funds to enable participation of visiting scientist Y. Yacoby in the experiments performed at the Advanced Photon Source]

7. Structure determination of monolayer-by-monolayer grown $La_{1-x}Sr_xMnO_3$ thin films and the onset of magnetoresistance, R. Herger, P. Willmott, C. Schlepuetz, M. Bjoerck, S. Pauli, D. Martoccia, B.D. Patterson, D. Kumah, R. Clarke, Y. Yacoby, M. Doebeli,   Phys. Rev. B **77**, 085401 (2008).

"We are indebted to E. Dagotto for his invaluable comments on the manuscript. Fruitful discussions with O. Bunk and J. Krempasky are gratefully acknowledged. We thank S. Weyeneth from the University of Zürich, Switzerland, for his assistance in the resistivity measurements and his help in interpretation of the results. Support of this work by the Schweizerischer Nationalfonds zur Förderung der Wissenschaftlichen Forschung and the staff of the Swiss LightSource is gratefully acknowledged. This work was partly performed at the Swiss Light Source, Paul Scherrer Institut. Work at the University of Michigan was supported in part by U.S. Department of Energy Grant No. DE-FG02-06ER46273 and by U.S. National Science Foundation Physics Frontier Center Grant No. PHY-0114336."
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8. Wideband detection of transient solid-state dynamics using ultrafast fiber lasers and asynchronous optical sampling, Vladimir A. Stoica, Yu-Miin Sheu, David A. Reis, and Roy Clarke, Optics Express **16**, 2322 (2008).

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9. Mapping single-crystal dendritic microstructure in nickel-base superalloys with synchrotron radiation, Naji S. Husseini, Divine P. Kumah, Jian Z. Yi, Christopher J. Torbet, Dohn A. Arms, Eric M. Dufresne, Tresa M. Pollock, J. Wayne Jones, Roy Clarke, Acta Materialia, 56, 4715-4721 (2008).

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10. In Situ Imaging of High Cycle Fatigue Crack Growth in Single Crystal Nickel-Base Superalloys by Synchrotron X-Radiation, Liu Liu, Naji Husseini, Christopher Torbet, Divine Kumah, Roy Clarke, Tresa Pollack, and J. Wayne Jones, J. Mtls. Eng. & Technology 130 (2008).

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[work supported mainly by AFOSR; DE-FG02-06ER46273 supported grad student D. Kumah, who participated in the experiments at Advanced Photon Source]

11. Strain and Composition Mapping of Epitaxial Nanostructures, C.N. Cionca, A. Riposan, D.P. Kumah, N.S. Husseini, D.A.Walko, Y. Yacoby, J. Mirecki Millunchick, and R. Clarke, Applied Physics Letters **92**, 151914 (2008).

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[participants in the experiment were supported from multiple sources. DE-FG01-06ER46273 supported the PI and postdoc C. Cionca, and NSF-DMR 0606048 supported A. Riposan. This was necessitated by the need to provide sufficient manpower to cover continuous data collection at the Advanced Photon Source]

12. Structural Changes Induced by Metal Electrode Layers on Ultrathin $BaTiO_3$ Films, Y. Yacoby, C. Cionca, N. Husseini, A. Riposan, J. Olmsted Cross, C. Brooks, D. Schlom, and R. Clarke, Phys. Rev. B 77, 195426 (2008).

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13. Growth and magnetic characterization of Co nanoparticles obtained by femtosecond pulsed laser deposition, A. Cebollada, J. M. García Martín, R. Asenjo and C. Clavero, Ll. Balcells, S.

Estradé, J. Arbiol, F. Peiró, C. Smith, R. Clarke, L. Martínez, Y. Huttel, E. Román, N. D. Telling, G. van der Laan, Phys. Rev. B**79** 014414 (2009).

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4. Ph.D. Dissertations:

Yongsoo Yang, "Structure of complex oxide interfaces" University of Michigan (defended March 10, 2014).
Nancy Senabulya, "Synchrotron X-ray studies at epitaxially strained interfaces" (obtained Candidacy, 9/6/2013; due to graduate April 2017).

5. Personnel Contributing to Research

The research involved primarily the PI's group, external collaborators and several visitors from international laboratories.

5.1 Postdoctoral Fellows in the Clarke Group:

- Christian Schlepütz now a Beam Line Scientist at APS).
- Vladimir Stoica, now a Research Fellow at Penn State University.

5.2 Graduate Students in the Clarke Group: (% support in brackets)

- Ibrahim Oraiqat – Graduated December 2015. Research topic: "Nanocrystalline solar cell materials made by ultrafast laser ablation." (0% -Fellowship); now a postdoc in UM Department of Radiation Oncology.
- Yongsoo Yang: Ph.D. Candidate until March 2014 (100%); Dissertation topic: Direct methods x-ray studies of oxide interfaces; now a postdoc at UCLA.
- James Mathis – Candidate for Ph.D. degree (0% - Fellowship)
- Nancy Senabulya -Candidate for Ph.D. degree (0% - Fellowship)
- Christina Jones -Candidate for Ph.D. degree (0% -Fellowship)

5.3 Undergraduate Researchers in the Clarke Group:

- Isabel Bonachera Martin (0%)

5.4 Collaborating Researchers

- Prof. Yizhak Yacoby, Danziger Prof. of Physics, Hebrew University, Jerusalem, Israel (travel)
- Stephen Durbin, Western Michigan University (0%)
- Carolina Adamo, Stanford University, NY (0%).
- Hans Christen, Oak Ridge National Lab (0%)
- Darrell Schlom, Cornell University (0%)