

AFRL-AFOSR-UK-TR-2014-0038



The possibility of improved and higher T_c superconductors in hybrid systems

**Gertjan Koster
Debakanta Samal**

**UNIVERSITEIT TWENTE
DRIENLLOLAAN 5
ENSCHDE, 7522 NB NETHERLANDS**

EOARD Grant 10-3077

Report Date: October 2014

Final Report from 15 July 2010 to 14 July 2014

Distribution Statement A: Approved for public release distribution is unlimited.

**Air Force Research Laboratory
Air Force Office of Scientific Research
European Office of Aerospace Research and Development
Unit 4515, APO AE 09421-4515**

REPORT DOCUMENTATION PAGE

Form Approved OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.
PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.

1. REPORT DATE (DD-MM-YYYY) 15 October 2014	2. REPORT TYPE Final Report	3. DATES COVERED (From – To) 15 July 2010 –14 July 2014
---	---------------------------------------	---

4. TITLE AND SUBTITLE The possibility of improved and higher Tc superconductors in hybrid systems	5a. CONTRACT NUMBER FA8655-10-1-3077
	5b. GRANT NUMBER Grant 10-3077
	5c. PROGRAM ELEMENT NUMBER 61102F

6. AUTHOR(S) Gertjan Koster Debakanta Samal	5d. PROJECT NUMBER
	5d. TASK NUMBER
	5e. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) UNIVERSITEIT TWENTE DRIENLLOLAAN 5 ENSCHDE, 7522 NB NETHERLANDS	8. PERFORMING ORGANIZATION REPORT NUMBER N/A
--	--

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) EOARD Unit 4515 APO AE 09421-4515	10. SPONSOR/MONITOR'S ACRONYM(S) AFRL/AFOSR/IOE (EOARD)
	11. SPONSOR/MONITOR'S REPORT NUMBER(S) AFRL-AFOSR-UK-TR-2014-0038

12. DISTRIBUTION/AVAILABILITY STATEMENT
Distribution A: Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

This project is a study of engineering 2d heterostructures to mimic the structure of bulk high temperature cuprate superconductors. Since these consist of CuO2 planes separated by charge reservoir layers, we attempt to use pulsed-laser deposition to generate alternating Sr and CuO2 planes. We succeeded in creating structures of charge-neutral SrO and CuO layers, which exhibited a relatively high-Tc superconductive transition. Additionally, investigation of the structure of these films shows that they have a stabilized rock-salt structure similar to MnO, FeO, CoO and NiO structures (different from the usual CoO monoclinic structure) which may make it a candidate for doping experiments.

15. SUBJECT TERMS

EOARD, hybrid systems, superconductors

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT SAR	18, NUMBER OF PAGES 7	19a. NAME OF RESPONSIBLE PERSON Victor Putz
a. REPORT UNCLAS	b. ABSTRACT UNCLAS	c. THIS PAGE UNCLAS			19b. TELEPHONE NUMBER (Include area code) +44 (0)1895 616013

Grant FA8655-10-1-3077

"The possibility of improved and higher T_c superconductors in hybrid systems"

Start date June 1st, 2011

Final date May 1st, 2014

Researcher Debakanta Samal.

Achievements:

Dr. Samal has started using the PLD equipment and is familiarizing himself with the characterization tools such as XRD, AFM and PPMS.

-First deposition of Sr₂RuO₄ thin films. P-wave superconductor for heterostructures with other symmetry superconductors.

-First deposition of tetragonal CuO. A series will be prepared for analysis by XMLD in order to verify the Neel temperature of this metastable phase. In principle it should be higher than tenorite, pointing to a possible higher T_c upon doping.

Project description:

The goal is to search for T_c enhancement by proximity in hybrid thin film systems. The samples under investigation are, for example, artificially layered heterostructures, whereby doping is varied in a controlled manner across interfaces going from underdoped on one side of the interface to overdoped on the other side. In order to be successful one has to be able to create atomically sharp interface, without cation intermixing. One can think of samples with single interfaces and samples with multiple interfaces, through multilayering.

The Twente group has an excellent track record on the fabrication of such multilayer structures by means of Pulsed Laser Deposition, monitored by high pressure RHEED. The advantage of PLD is the flexibility of materials systems that can be chosen, therefore making a quite extensive search possible. The group has shown in the past that even meta-stable crystal structures can be made in the case of multi layering of the infinite layer compounds ACuO₂ where A=Ba, Sr, Ca, and block-by-block synthesis of YBCO systems, where charge neutral blocks are deposited sequentially with the overall stoichiometry of the compound that has to be formed, pointing to the multitude of possibilities.

Proof of principle will be achieved when T_c 's are measured which exceed the value of the optimally doped parent compounds. However, extensive experimental procedures have to be implemented to establish the true nature of the enhancement, whether it be chemical, physical or both, if successful.

Systems that are of interest are:

1. Another route to achieve aforementioned heterostructures is by looking at phase separated thin films where regions of overdoping and underdoping can be found. In such case local scanning probes would have to be implemented to probe local variations in T_c . A means to control this phase-separation would be by looking carefully at crystal termination planes, where growth kinetics depends upon which crystal plane forms the topmost layer of the crystal. ⁱ
2. Superconducting, -non-superconducting interfaces interfaces with multiband superconductors

Achievements:

(a) Experimental evidence for Cu-O chain-like structural transformation in ultra-thin films of polar infinite layer SrCuO₂:

In common, the structural paradigm of high temperature cuprate superconductors is found to consist of CuO₂ planes separated by charge reservoir layers. Such structural model continues to spur researchers to artificially tailor-make likewise structures that can exhibit superconductivity. However, it has always been a hard-nut to control and measure the structure

of the oxygen sub-lattice precisely in thin films and heterostructures; which plays a pivotal role to influence the structure-property affair in complex oxide thin films. We have focused our study to effectively control the oxygen position surrounding the copper ion in ultrathin cuprate films and look for new electronic functionality in the cuprate based heterostructures.

The parent structure of tetragonal SrCuO₂ (SCO) consists of dipole like oppositely charged alternating Sr²⁺ and CuO₂⁻² planes and hence polar in nature. The electrostatic energy due to the existing dipole-like layers in polar systems depends on the film thickness and, when it is too large, the thin film system responds to it either by electronic redistribution or atomic re-arrangement. We demonstrate with detailed structural and spectroscopic investigation that by varying precisely the thickness of SCO layers grown on SrTiO₃, one can re-arrange the oxygen ions. In particular, we show that it is possible to move the oxygen ion from CuO₂ plane to Sr plane and, thereby making the structure to consist of charge neutral SrO and CuO layers. This phenomenon turns out to be a direct response of a polar cuprate system to electrostatic instability and reveals that the oxygen sub-lattice in cuprates can be effectively engineered giving each layer a specific function, for example, current-carrying layers, charge reservoirs and scaffolding layers. From magnetic point of view, the plane and chain-type SrCuO₂ layers exhibit sharply distinct behavior in terms of their magnetic excitations as observed from RIXS. Besides, we have demonstrated the realization of high-T_c superconductivity (Fig.5) in the artificial cuprate based heterostructures, where the chain-like ultrathin layer is sandwiched between planar layers (mimicking the structural model in bulk cuprates). The spectroscopic signature for Zhang-Rice singlet indicates hole doping for the observed superconductivity. However, it has to be emphasized that when the chain like cuprate layer is replaced by ultrathin perovskite layers such as SrTiO₃ or SrRuO₃, the superconductivity is not found. (Fig.4).

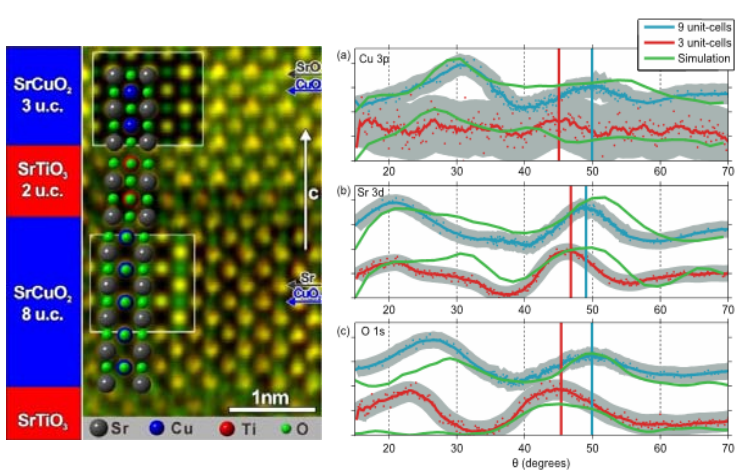


Fig.1

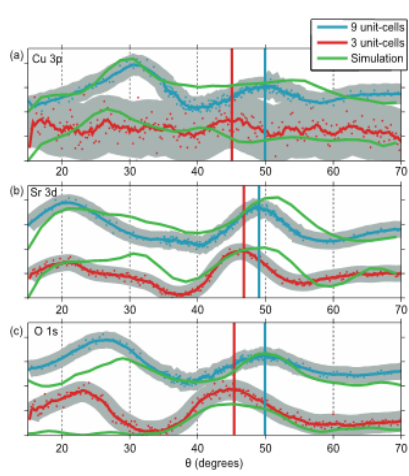


Fig.2

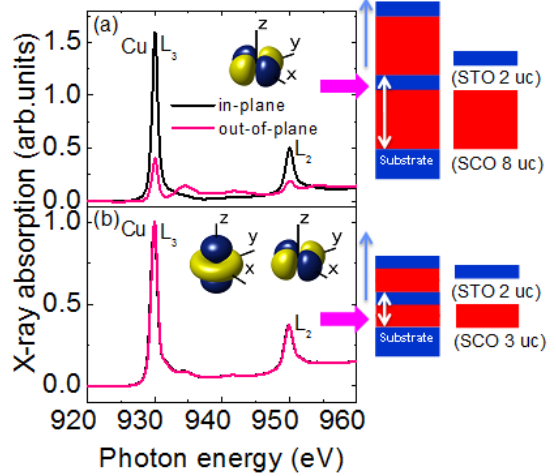


Fig.3

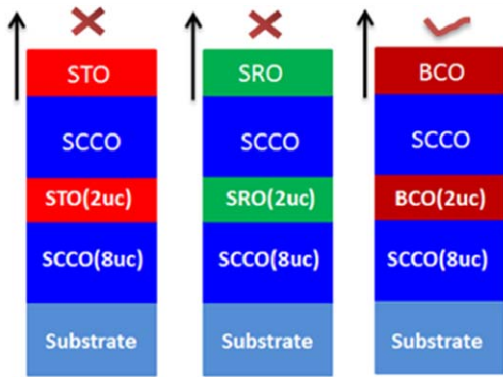


Fig.4

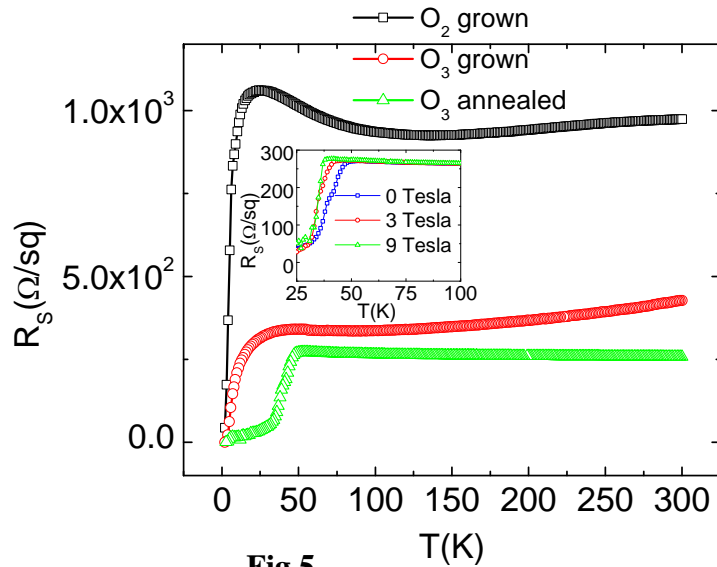


Fig.5

Captions: Fig.1 shows the scanning transmission electron microscopy (STEM) image that clearly distinguishes the presence of apical oxygen in the 3 unit cell (uc) chain-type SrCuO₂ layer as opposed to the planar 8 uc SrCuO₂ layer. Fig.2 shows the results of X-ray photo electron diffraction study between chain-type (3 uc) and plane type (9 uc) SCO layers. Clearly, an increase in c-axis lattice parameter is observed for 3 uc SCO layer as compared to 9 uc layer. Fig.3 shows the polarized X-ray absorption spectra illustrating the distinct difference in the hole occupation with respect to the SCO layer thickness. Fig.4 shows the schematic of the superlattice structures: [SCCO(8uc)/STO(2uc)]₁₀, [SCCO(8uc)/SRO(2uc)], and [SCCO(8uc)/BCO(2uc)]₁₀; where the superconductivity is only observed for [SCCO(8uc)/BCO(2uc)]₁₀. Fig.5 shows the observed superconductivity for [SCCO(8uc)/BCO(2uc)]₁₀ under different growth conditions and the inset shows the same under application of magnetic field.

(b) Investigation on crystal/electronic structure and magnetism of the novel tetragonal ultra-thin CuO films:

The CuO in its bulk form is at variance in crystal structure and magnetic properties as compared to other transition metal monoxides in the same family. While MnO, FeO, CoO and NiO are stabilized in the rock salt crystal structure, CuO stabilizes itself in the monoclinic phase with relatively lower antiferromagnetic Neel temperature. Were it in the form of rock-salt structure, it would have been a potential candidate for doping experiment to look for high T_c superconductivity. Our investigation on the growth of ultrathin CuO films reveals the stabilization of a tetragonal rocksalt structure with an elongated c -axis such that $c/a \sim 1.34$ and the Cu-O-Cu bond angle $\sim 180^\circ$, pointing to a metastable six-fold coordinated Cu. X-ray absorption spectroscopy demonstrates that the hole at the Cu site for the CuO is localized in $3d_{x^2-y^2}$ orbital unlike the monoclinic CuO bulk-phase. The experimental confirmation of the tetragonal structure of CuO opens up new avenues to explore electronic and magnetic properties of six-fold coordinated Cu. Indeed, our preliminary investigation using RIXS indicates the antiferromagnetic ground state for this novel phase. However, further studies are underway to unravel the details. Besides, interfacial doping experiments are underway to realize the possibility for high T_c superconductivity in this novel phase of CuO.

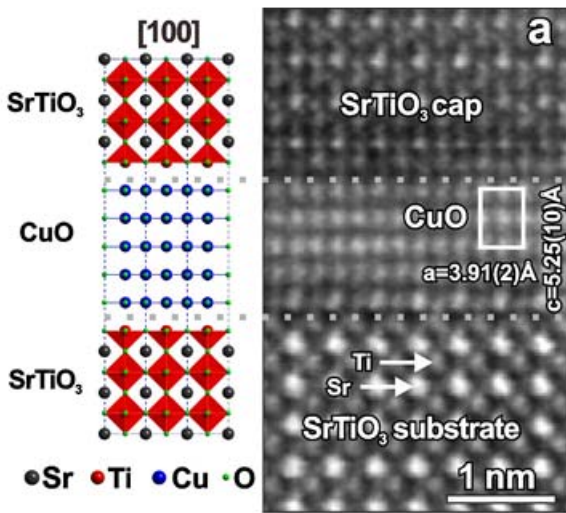


Fig.6

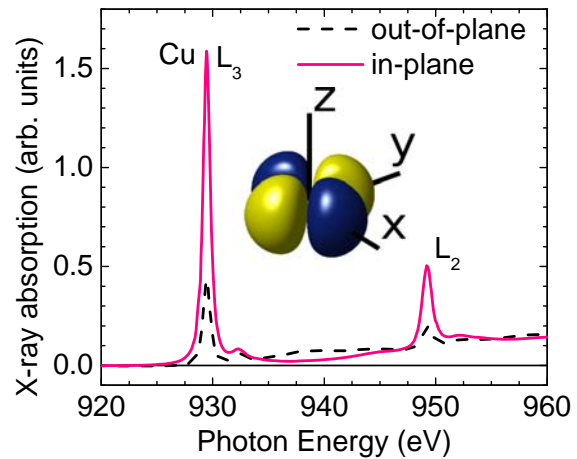


Fig.7

Captions: Figure 6: STEM image of an ultrathin tetragonal CuO film along the [100]. A tetragonal structure model matching the observations is shown on left side of Fig.6. Fig.7 shows the polarized X-ray absorption spectra for a tetragonal CuO film. The inset shows the schematic for the $d_{x^2-y^2}$ orbital where the hole at the Cu site is preferentially localized.

Output in term of publications:

1. D. Samal, G. Koster, *et al.*, Phys. Rev. Lett., 111, 096102 (2013)
2. B. Kuiper, D. Samal, G. Koster, *et al.*, APL Mater. 1, 042113 (2013) (*Editor's pick*)
3. D. Samal, G. Koster, *et al.*, Europhysics Letter, 105, 17003, (2014)
4. D. Samal and G. Koster, Manipulating oxygen sub-lattice in ultrathin cuprates: A new direction to engineer oxides (*To appear as an invited feature paper in Journal of materials research, 2014*)
5. Proximity induced superconductivity in infinite-layer based cuprate heterostructures: the role of spacer layer? D Samal, G. Koster, *et al.*, (*to be submitted*)
6. A comparative study of magnetic excitations using RIXS for plane versus chain type SrCuO₂ layer. (*in preparation along with collaborators*)

Oral presentation in conferences/meeting:

1. "Novel structural transformation in the ultrathin films of cuprates and its influence on electronic and magnetic properties, **APS March Meeting, March 18–22, 2013, Baltimore, Maryland, USA.**
2. "Manipulating oxygen sub-lattice in ultra-thin cuprates: A new direction to engineer oxides" **2014 MRS Spring meeting, April 21-25, 2014, San Francisco, California, USA.**
3. "Controlling oxygen sublattice in ultrathin polar cuprates: a new direction to engineer oxides" **Physics@FOM, 21-22, January, 2014, Veldhoven, The Netherlands.**

Poster presentation:

- (1) "Experimental evidence for Cu-O chain-like structural transformation in ultra-thin films of polar infinite layer SrCuO₂" at (i) Innovations in Strongly Correlated Electronic Systems: School and Workshop, Aug 6-17, 2012, ICTP, Trieste, Italy and (ii) Oxide electronics 19, Sep 30-Oct-03, 2012, Apeldoorn, Netherlands
- (2) "Novel structural transformation in ultrathin cuprates" at China/ US Winter School & 3rd China/US workshop on Novel Superconductors, Jan 19-27, 2013, Hongkong.
- (3) "Controlling oxygen sub-lattice in ultrathin cuprates: A new direction to engineer oxides" at workshop on Oxide Electronics 20, Sep 22-25, 2013, National University of Singapore.
- (4) "Forced-epitaxy induced high symmetry CuO: What novel electronic property we can expect from?" Superconductivity and Magnetism at the Nanoscale, June 30 -July 3, 2014, Stuttgart, Germany

¹ H. Zheng, J. Wang, S. E. Lofland, Z. Ma, L. Mohaddes-Ardabili, T. Zhao, L. Salamanca-Riba, S. R. Shinde, S. B. Ogale, F. Bai, D. Viehland, Y. Jia, D. G. Schlom, M. Wuttig, A. Roytburd, R. Ramesh, Multiferroic BaTiO₃-CoFe₂O₄ Nanostructures, *Science* 303, (2004) 661