LABORATORY DIRECTED RESEARCH AND DEVELOPMENT
TOWARDS IN-SITU GROWTH AND SPECTROSCOPY OF COMPLEX OXIDE
THIN FILMS AND HETEROSTRUCTURES

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<td>Proposal Term</td>
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Abstract

This project proposes the initiation of a new strategic direction within SLAC, to bridge advanced complex oxide thin film and heterostructure growth techniques with in situ characterization capabilities. A mobile pulsed laser deposition (PLD) system will be implemented to be compatible with surface chemistry, soft x-ray, and ARPES beam-lines at SSRL.

Summary of Proposal

Description of Project

The ability to grow and engineer complex oxide thin films and heterostructures on an atomic scale has made tremendous advances over the past decade. These capabilities for materials design have the potential to broadly impact fundamental science by the creation of emergent phenomena, and the control of the electronic structure of correlated materials. Furthermore, the use of oxides for energy applications can be greatly enhanced by designing the band alignments, interfaces, and surfaces relevant for fuel cells, catalysis, and photovoltaics.

While many photon probes exist at SLAC for the study of these problems, there are currently no oxide thin film growth capabilities that can be linked in situ, which is vital given the surface sensitivity of many of the relevant measurement techniques. This project will develop a mobile ultra-high vacuum PLD chamber, designed to be compatible with existing and near future beam-lines at SSRL.

Expected Results

A new pulsed laser deposition system will be developed, the first such capability at SLAC, and housed in the SIMES laboratories currently completing renovation. Here materials growth can be optimized in advance of installation for in situ measurements. The focus of this project will be integration and demonstration of in situ ARPES (BL 5-4; BL 5-2 currently under construction) and soft X-ray spectroscopy (BL 13-2). Subsequently, it can be adapted for other in situ experimental activities, including other beam-lines and potentially scanning tunneling microscopy (STM). These capabilities will allow for short-term in situ experiments at SLAC, which will develop our expertise and inform decisions for fixed growth installations currently under consideration.
Proposal Narrative

Purpose/Goals

In the context of research on electronic and atomic reconstructions of oxide heterointerfaces, there is a compelling scientific opportunity to probe the electronic states and reconstructions of pristine thin films surfaces, and their coupling to proximate interfaces. A major limitation of surface science techniques applied to complex oxides thus far has been the difficulties with their surface preparation. The same complexity which gives rise to the rich chemistry and physics of these materials is manifest at their surfaces, and much of the high impact research has been limited to the small class of compounds which cleave easily, such as layered cuprate superconductors. This is self-consistent, in that well-defined cleavage planes in these ionic materials general arise when there are weak or van der Waals forces between structural units. This means that the surface is a weak perturbation from the bulk, and ARPES and STM can provide information relevant for the bulk electronic structure.

The frontiers of research we focus on here, however, are precisely the cases for which the interface or surface (interface with vacuum) creates a strong perturbation, driving a reconstruction which fundamentally alters the electronic structure from bulk form. These arise from imposed electrostatic boundary conditions such as polar surfaces and interface discontinuities, their atomic reconfigurations, and the strong interplay between electronic structure, polar distortions, and orbital degrees of freedom. Many of the novel phenomena recently discovered at oxide heterointerfaces – metallic, superconducting, and magnetic states between insulators – can also be expected surfaces. However, without the ability to probe them in pristine form, in situ, virtually all of the relevant information is lost ex situ. Indeed the state itself may be lost by contamination, surface compensation, etc. By combining both growth and spectroscopy together, we can access a wealth of possibilities.

Approach/Methods

Pulsed laser deposition chamber: This will be the central in-situ facility for fabricating oxide thin films, with atomically controlled surfaces and interfaces. PLD is a versatile growth technique in which a pulsed, high power ultraviolet laser is focused or imaged onto a solid target inside the chamber. With each pulse, material is energetically ablated and deposited on the heated substrate. PLD is highly suited to growing complex oxides, since in many cases it can preserve the cation stoichiometry of the target (while oxygen partial pressure is provided in the growth chamber). Further cation control can be achieved by tuning the radial distribution within the plume. Aspects of the design are
based on existing systems, with a number of modifications necessary for in situ integration. The key technical features are as follows:

- **IR laser heater**: Rather than the more typical resistive or radiative lamp heater, the substrate will be heated by an infrared solid-state laser external to the chamber, fiber coupled and imaged into the chamber onto the substrate holder. This design removes the heat source to outside the chamber, greatly reducing the physical infrastructure and size needed within the chamber to support the substrate. In particular, this allows a minimal thermal mass involved in the heater assembly, allowing for rapid thermal quenching and minimal component out-gassing. These are both vital for preserving a pristine surface for transfer to the STM and ARPES stations.

- **Differentially pumped electron gun**: The key in-situ monitoring tool during growth is reflection high-energy electron diffraction (RHEED), in which a grazing incidence electron beam (15-30 keV) is used for surface diffraction, and for monitoring the periodic surface roughening and smoothening associated with layer-by-layer growth. The technical challenges of observing RHEED in high pressure reactive oxygen are addressed by using a differentially pumped electron gun and by minimizing the electron path length at high pressures (internal screen). For high precision structures, the two-dimensional growth mode is used to directly monitor the deposition of each unit cell, allowing the growth of layers and interfaces with atomic precision. The tradeoff in using an IR laser heater is that the substrate position is now fixed due to the sensitivity of the coupling optics. Therefore the electron beam is steered by coils rather than physically positioned.

 TARGET beam-lines for integration:

- **BL 5-4 (and future BL 5-2)**: ARPES has emerged as a leading experimental probe for studying quantum materials, a subject of increasing importance. The existing 5-4 branch line features a normal incidence monochromator (NIM) that covers a photon energy range of 7-35 eV with a resolving power of more than 20,000. Together with a SCIENTA R4000 analyzer, this branch line is dedicated for high resolution ARPES experiments in the low photon energy range. The ARPES end station is equipped with a low temperature manipulator covering 5-400K and LEED.

To realize the full potential of ARPES and to capitalize the new capabilities presented by the SPEAR3 upgrade and its pending operation at 500 mA, a new complementary undulator branch line (5-2) is currently under construction covering the photon energy range of 20-150 eV. It will completely modernize and greatly expand the capabilities of the existing NIM branch-line with more polarization control and extended photon energy range, as well as significant improvement in flux and beam spot size.
• **BL 13-2:** This is a variable polarized undulator beamline, which is ideal for the study of the surface of in-situ grown films. The end station has soft X-ray emission spectroscopy (C, N, and O K-edge), soft X-ray absorption spectroscopy (C, N, and O K-edge and 3d transition metal L-edge) and soft X-ray photoemission spectroscopy.

**Specific Location of Work**

This work will be permanently housed in the SIMES laboratories at SLAC, and on a temporary basis on the SSRL beam-lines identified above.

**Anticipated Outcomes/Results**

While the primary technical goal is the demonstration of in situ growth and spectroscopy, the scientific research goals are the following:

1. Demonstrate the atomic termination-layer dependence of the surface electronic structure of perovskites, and the compensating electronic reconstructions induced.
2. Probe the dimensional crossover in the electronic structure as a 3D perovskite is artificially driven 2D in an ultra-thin film.
3. Investigate the termination layer dependence of surface photo-catalytic activity of complex oxides.

**Brief Report of Results to Date & Summary of 2nd Year Plans**

Thus far, a chamber has been set up on campus, and we will shortly begin installation and testing in the newly renovated SIMES lab space in Bldg. 40. Scientifically, we have of course only been able to do ex situ experiments until now, but have pursued 2 directions to develop the collaborations and expertise required here:


2. Based on our unexpected finding of interface electronic structure control by surface adsorbates (Y. W. Xie, Y. Hikita, C. Bell, H. Y. Hwang, “Control of Electronic Conduction at an Oxide Heterointerface Using Surface Polar Adsorbates,” *Nature Communications* **2**, 494 (2011)), we did an initial ex situ experiment on BL 13-2. Unfortunately, the lightning strike of April 12, 2012 terminated the experiment, but preliminary results clearly indicate a massive reconstruction under exposure to water vapor, which will be pursued further.

In the 2nd year, our focus will be to set up growth capabilities in Bldg. 40, continue to work with BL 5-2 construction progress to ensure compatibility, and we hope to have a 1st opportunity to try a run with in situ growth and spectroscopy on BL 13-2.
VITA (Lead Scientist)

HAROLD Y. HWANG

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PROFESSIONAL PREPARATION
Princeton University Physics PhD, 1997
Massachusetts Institute of Technology Electrical Engineering (BS, MS); Physics (BS), 1993

APPOINTMENTS
Professor, Stanford University (Applied Physics & SLAC Photon Science, 2010 - present)
Professor (Assoc.; Full), Univ. of Tokyo (Advanced Materials & Applied Physics, 2003 - 2010)
Member of Technical Staff, Bell Laboratories (Materials Physics Research, 1996 - 2003)

RESEARCH INTERESTS
Novel devices based on interface states in oxides; Probing correlated electrons at artificial interfaces and in confined systems; Atomic scale synthesis of complex oxide heterostructures.

SELECTED PUBLICATIONS (>140; 4 book chapters; 8 patents; h index=39; >9,000 citations)

AWARDS
APS Fellow (2011)
IBM Japan Science Prize (Physics, 2008)
Materials Research Society Outstanding Young Investigator Award (2005)
Budget

The LDRD budget includes costs of personnel, travel, capital equipment, and materials and services totalling $333.3k in FY13 and $333.3k in FY14. The budget includes salary for PI, Harold Hwang, at 1% and 30% for associate staff scientists Yasuyuki Hikita. It also includes support for 100% of one postdoc. Materials and services are projected at $142k in FY13 and $100.5k in FY14. We request $4k each year for travel so the PI and associate staff scientists may present results from this project at national conferences. Please see accompanying Excel budget for details.

Approvals

Stephanie Carlson, Acting Business Manager PSD

Tom Devereaux, Director, SIMES

Cynthia Friend, ALD, Photon Science